Iminyls. Part 4.[1] Intramolecular Abstraction of Benzylic Hydrogen by Diaryliminyls

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Diaryliminyls, generated in aqueous solution by oxidation of imino-oxyacetic acids with persulphate abstract hydrogen from primary and secondary *ortho*-alkyl substituents to give benzylic radicals. These mainly cyclise (before or after oxidation to the corresponding carbonium ions) to oxoanthryl and/or isoindoleninyl products which are further oxidised by the persulphate. *o*-Methyl- and *o*-ethyl-diaryliminyls, generated by thermolysis of t-butyl peracetates in benzene react to give mainly the corresponding imine (and/or ketone by hydrolysis). Intramolecular hydrogen transfer occurs with *o*-isopropyl- and *o*-benzyl-diaryliminyls, the resulting benzyl radicals reacting further to give 10,10-dimethylanthrone and 1,3-diphenyl-2-(10-phenyl-9-anthryl)isoindole (and products derived therefrom), respectively. The e.s.r. spectra of several of the iminyls have been detected.

1,5-Hydrogen transfers are the most frequently encountered shifts in free radical chemistry, and have been observed with carbon, nitrogen, oxygen, and other hetero radicals.[2] The six-membered transition state through which such transfers proceed allows near collinearity of the three reacting centres, and is apparently more favourable than smaller or larger cyclic transition states. Aryliminyls should undergo such reactions with ease since the >C=N· group can remain in conjugation with the aryl ring during the transfer process. Despite this favourable factor there is only one probable example of an *o*-hydroxyphenyl(phenyl)iminyl abstracting hydrogen from the adjacent hydroxy group.[3] In this paper we report on the intramolecular transfer of benzylic hydrogen to the iminyl function of diaryliminyls.

(1) *Oxidation of Imino-oxyacetic Acids with Persulphate.*—The homologous series of *o*-alkyldiphenylmethyleneamino-oxyacetic acids (1; R = H, Ar = *o*-MeC_6H_4, *o*-EtC_6H_4, *o*-$Pr^iC_6H_4$, and 2,4-$Me_2C_6H_3$), the *o*-benzyl analogue (1; R = H, Ar = *o*-$PhCH_2C_6H_4$), and the 2-methylpropanoic acids (1; R = Me, Ar = *o*-MeC_6H_4 and 2,4-$Me_2C_6H_3$) were readily oxidised by persulphate in boiling aqueous solution to give a wide variety of products (Table 1). These arise (a) directly from the corresponding iminyl (type a); (b) by dimerisation or intramolecular cyclisation of benzyl radicals formed from the iminyls by intramolecular hydrogen abstraction (type b); (c) by cross-coupling of iminyl, benzyl, or other intermediate radicals generated during the oxidation (type c).

TABLE 1

Yields (%) of products from imino-oxyacetic acids (1) and (2)

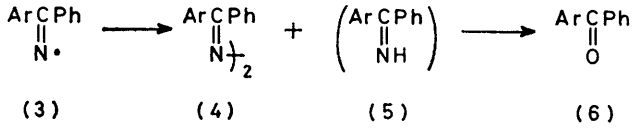
Substrate	Ketone (6)	Azine (4)	Bibenzyl (9)	Anthrone (12) or (16)	Anthraquinone (14)	Blue pigment (13)	Other products
(1; Ar = *o*-MeC_6H_4, R = H)	23	1	5		23	1.5	4.3 (25; $R^1 = R^2 = R^3 = H$)
(1; Ar = *o*-MeC_6H_4, R = H) *	29	*ca.* 1	*ca.* 5		*ca.* 23		8 (19; $R^3 = H$) 6 (18; $R^3 = H$) *ca.* 4 (25; $R^1 = R^2 = R^3 = H$)
(1; Ar = *o*-MeC_6H_4, R = Me)	*ca.* 23	*ca.* 1	*ca.* 5		*ca.* 23		*ca.* 4 (25; $R^1 = R^2 = R^3 = H$)
(1; Ar = 2,4-$Me_2C_6H_3$, R = H)	16	1	3		11	1.3	9 (25; $R^1 = R^2 = H$, $R^3 = Me$)
(1; Ar = 2,4-$Me_2C_6H_3$, R = Me)	20	†	5		3		3.5 (25; $R^1 = R^2 = H$, $R^3 = Me$)
(1; Ar = 2,4,6-$Me_3C_6H_2$, R = H)		22					
(1; Ar = 2,4,6-$Me_3C_6H_2$, R = Me)		20					
(1; Ar = *o*-EtC_6H_4, R = H)	†			46	1		
(1; Ar = *o*-$PhCH_2C_6H_4$, R = H)				35			8 (20; $R^1 = Ph$, $R^2 = R^3 = H$) 2.5 (22; $R^1 = Ph$, $R^3 = H$) 1.5 (24; $R^1 = Ph$, $R^3 = H$)
(1; Ar = *o*-$Pr^iC_6H_4$, R = H)	†			97			
(1; Ar = *o*-$MeOC_6H_4$, R = H)	†	88					
(2; R = Me, Ar = *o*-MeC_6H_4)			21				
(2; R = Bu^t, Ar = *o*-MeC_6H_4)							53.5 ‡

* In the presence of Cu^{II} ions. † Detected by t.l.c. but not isolated. ‡ *o*-Toluonitrile.

(1)

(2)

Formation of type a products. Unlike diphenyliminyl,[4] *o*-alkylphenyl(phenyl)iminyls dimerise to azines only to

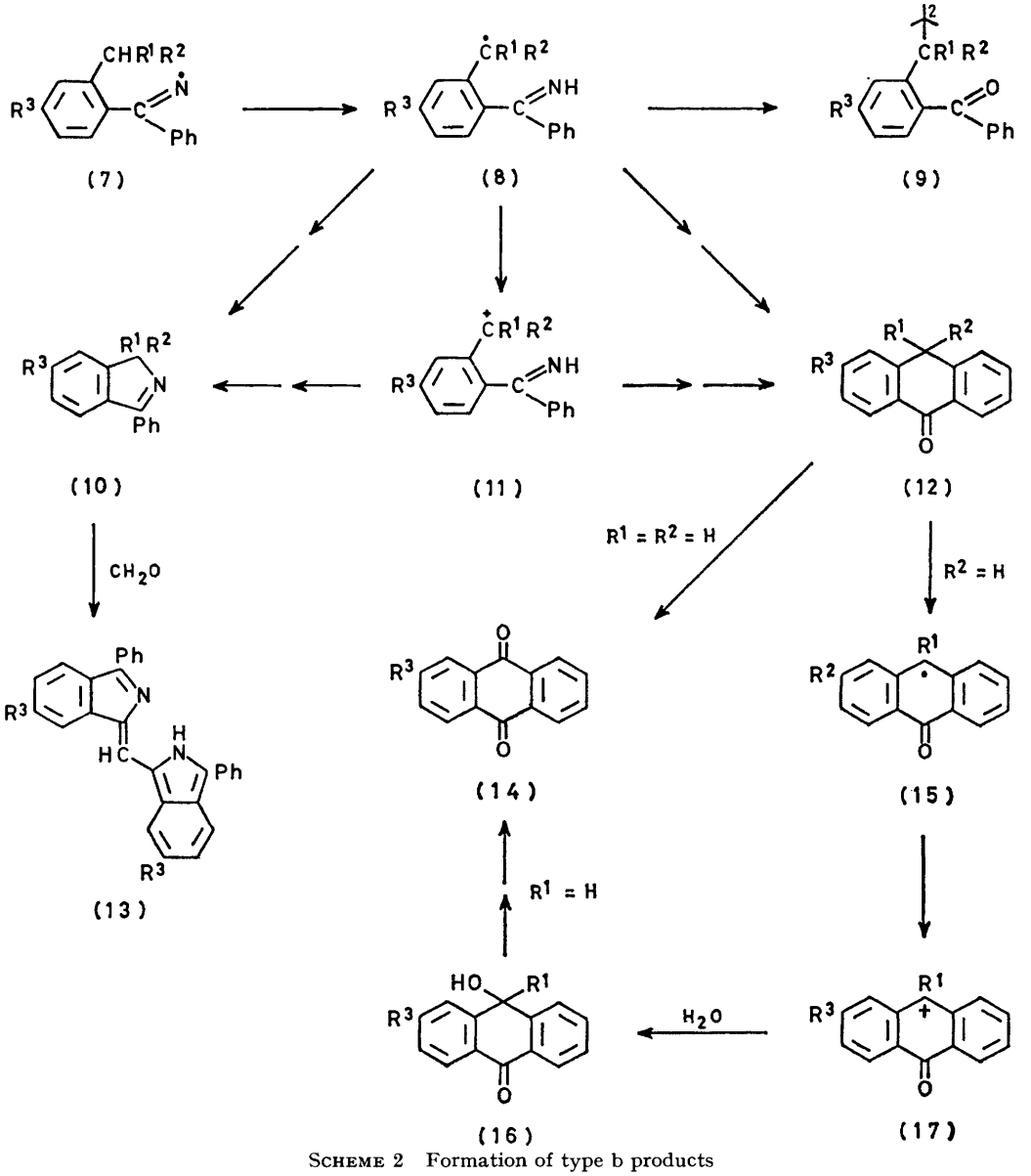


(3) (4) (5) (6)

SCHEME 1 Formation of type a products

a small extent or not at all (Table 1). Since *o*-methoxyphenyl(phenyl)iminyl (3; Ar = *o*-$MeOC_6H_4$) similarly generated, dimerises efficiently to the azine (4; Ar = *o*-$MeOC_6H_4$) (88%) this difference is due, not to increased steric protection of the iminyl by the *o*-alkyl substituent, but to the more favourable intramolecular hydrogen abstraction. Intermolecular hydrogen abstraction, as measured by ketone (6) formation [*via* hydrolysis of the imine (3) → (5) → (6)], is only significant (*ca.* 20%) for *o*-methylphenyl- and 2,4-dimethylphenyl-(phenyl)-iminyls (3; Ar = *o*-MeC_6H_4 and 2,4-$Me_2C_6H_3$) and decreases with increasing ease of intramolecular hydrogen abstraction ($PhCH_2 > Me_2CH \approx MeCH_2 > Me$).

Formation of type b products. Dimerisation of the benzyl radicals (8) to the corresponding bibenzyl [giving (9) after hydrolysis of imine to ketone] only occurs to a measurable extent with the least hindered radicals (8; $R^1 = R^2 = H$, $R^3 = Me$, and $R^1 = R^2 = R^3 = H$). Formation of the anthraquinones (14; R^3 = H and Me)



SCHEME 2 Formation of type b products

and the blue isoindolenine pigments (13; R^3 = H and Me) from the acids (1; R = H, Ar = *o*-MeC_6H_4 and 2,4-$Me_2C_6H_3$), respectively, showed that there are at least two other reaction pathways available to the benzyl radicals (8; $R^1 = R^2 = R^3 = H$ and $R^1 = R^2 = H$, $R^3 = Me$). In one, the benzyl radical cyclises onto the

adjacent phenyl group to give, after aromatisation, and hydrolysis of the resulting imine, the anthrone (12; $R^1 = R^2 = H$) which is further oxidised by persulphate to the quinone (14). An analogous sequence of reactions occurs when *o*-benzoyltoluene is oxidised with t-butoxyl radicals.[5] In the other pathway, the benzyl radical (8) adds to the nitrogen of the imino group to give, after oxidation, the isoindolenine (10). Subsequent reaction of the isoindolenine (10) with formaldehyde in the weakly acidic persulphate solution then gives the blue pigment (13). Our mechanism for this last reaction is supported by the following: (i) the 2-methylpropanoic acids (1; R = Me, Ar = *o*-MeC_6H_4 and 2,4-$Me_2C_6H_3$) from which the iminyls are generated by oxidative loss of carbon dioxide and *acetone*, gave product mixtures which were similar to those obtained from the corresponding acetic acids (1; R = H, Ar = *o*-MeC_6H_4 and 2,4-$Me_2C_6H_3$) except for the absence of the blue pigments (Table 1), and (ii) a phenyl analogue of the blue pigment (13; R^3 = H) has been prepared previously by reaction of 1-phenylisoindolenine and benzaldehyde.[6] The blue pigment (13; R^3 = H) has also been prepared by reaction of phenylmagnesium bromide and *o*-cyano-β-bromostyrene,[7] and from *o*-acetylbenzophenone and ammonia.[8] Our product had properties identical with those described except that it readily gave a green acetyl derivative with acetic anhydride (*cf.* ref. 7).

An alternative route to the isoindolenine and anthraquinone products is *via* the carbonium ion (11) formed by oxidation of the benzyl radical (8) by persulphate. Formation of the isoindolenine by intramolecular trapping of the carbonium ion by the imino group is analogous to that of 3-phenylphthalide and 3-phenylphthalimide from *o*-carboxy- and *o*-carboxamido-benzyl carbonium ions,[9a] respectively, and there is ample precedent for electrophilic intramolecular aromatic substitution leading to the anthrone (12). There is the further possibility that anthrone formation involves benzyl radicals and isoindolenine formation benzylic carbonium ions or *vice versa*, the product distribution reflecting the ease of oxidation of the benzylic radical.

In order to distinguish between these possibilities the persulphate oxidation of the imino-oxyacetic acid (1; R = H, Ar = *o*-MeC_6H_4) was repeated with copper(II) ions (1 mol. equiv.) present to facilitate oxidation of the radical (8; $R^1 = R^2 = R^3 = H$) to the carbonium ion[9] (11; $R^1 = R^2 = R^3 = H$). Although the product mixture was similar to that obtained without copper(II) ions no blue pigment (13) and two new minor products, one orange, the other yellow, were formed. The coloured products are of type c and have been identified as (18) and (19) (see following section). Hence, the small but significant increase in proportion of isoindolenine-type products formed in the presence of copper(II) ions implies that these arise by cyclisation of the carbonium ion (11) and not of the radical (8). The absence of the blue compound further establishes the role of formaldehyde in its formation since the latter would be oxidised by the copper(II) ions.

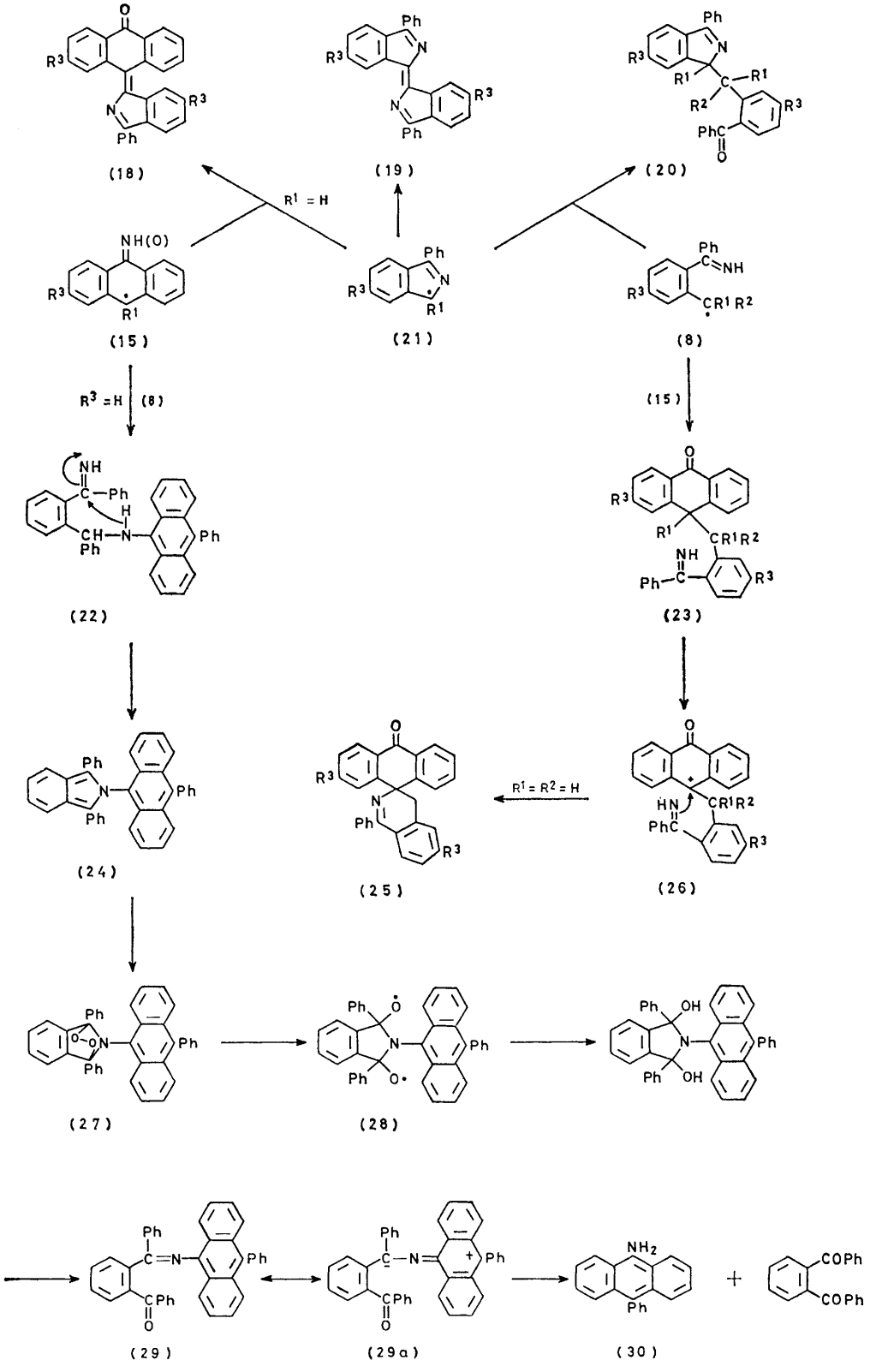
The major products obtained from the *o*-ethyl- and *o*-benzylphenyliminyls (7; R^1 = Me, $R^2 = R^3$ = H and R^1 = Ph, $R^2 = R^3$ = H) were the hydroxyanthrones (16; R^1 = Me, R^3 = H and R^1 = Ph, R^3 = H, respectively). These correspond to the anthraquinones (14) from the *o*-tolyl- and 2,4-dimethylphenyl-iminyls, the tertiary hydroxy groups in (16; R^3 = H, R^1 = Me or Ph) resisting further oxidation. The *o*-isopropylphenyliminyl (7; $R^1 = R^2$ = Me, R = H) gave the 9,9-dimethylanthrone (12; $R^1 = R^2$ = Me, R^3 = H) in almost quantitative yield. Hence, the yields of anthrone-derived products decrease as the oxidation level of the final product increases, *i.e.* (12; $R^1 = R^2$ = Me, R^3 = H) > (16; R^1 = Me, R^3 = H) > (16; R^1 = Ph, R^3 = H) > (14; R^3 = H).

Formation of type c products. Many of the oxidations (Table 1) gave minor products whose structures provide evidence for the mediation of oxoanthryl (15), benzyl (8), and isoindoleninyl (21) radicals.

The *o*-methyl- and 2,4-dimethyl-diphenylmethyleneimino-oxyacetic acids (1; R = H, Ar = *o*-MeC_6H_4 and 2,4-$Me_2C_6H_3$) gave the spiroanthrones (25; $R^1 = R^2$ = H, R^3 = H and Me) in low yield. Assignment of structure was based on molecular formula ($C_{20}H_{19}NO$ for R^3 = H) derived from elemental analysis and high resolution mass spectra, carbonyl absorption in the i.r. at 1 669 cm^{-1}, and ^1H n.m.r. signals at δ 3.18 (2 H), 7.82 (2 H), and 8.26 (2 H) which we assign to the methylene group, the *ortho*-protons of the phenyl group (*cf.* Part 3), and the *peri*-hydrogens of the anthrone moiety, respectively. The presence of a tertiary sp^3 hybridised carbon was confirmed by the singlet at δ 61.87 in its 'off-resonance' ^{13}C n.m.r. spectrum. Although these spiroanthrones could be formed in a number of ways we favour initial coupling of oxoanthryl (15) and benzyl (8) radicals with subsequent oxidative cyclisation of the product (23) as indicated in Scheme 3 [(23) ⟶ (26) ⟶ (25)].

The orange product obtained on oxidation of the acid (1; R = H, Ar = *o*-MeC_6H_4) in the presence of copper(II) ions had properties identical with those described for the bisisoindolenine (19; R^3 = H) (see Experimental section) formed on catalytic hydrogenation of *o*-benzoylbenzonitrile.[10] The accompanying yellow compound $C_{28}H_{17}NO$ has been identified as the anthronylidene derivative (18; R^3 = H) (see Experimental section). Formation of these two products suggests that isoindoleninyl radicals (21; R^3 = H), which presumably arise by oxidation of the isoindolenine (10),[11] are present in much higher concentration than in the corresponding oxidations without copper(II) ions present.

o-Benzyldiphenylmethyleneamino-oxyacetic acid (1; R = H, Ar = *o*-$PhCH_2C_6H_4$) gave three minor products. The colourless one, $C_{40}H_{20}NO$, which showed carbonyl absorption in the i.r. at 1 657 cm^{-1} and a singlet at δ 6.0 (1 H) in its n.m.r. spectrum is assigned structure (20; R^1 = Ph, $R^2 = R^3$ = H) and clearly must arise by coupling of isoindoleninyl (21; R^1 = Ph, R^3 = H) and benzyl radicals (8; $R^1 = R^2$ = H). The other two



SCHEME 3 Formation of type c products

have been identified as the yellow isoindole (22; R^1 = Ph, R^3 = H) and the orange imine (24; R^1 = Ph, R^3 = H). Their structures and formation are fully discussed in section (2).

Conclusions. Since type b and c products all have an isoindolenine (or isoindole) and/or oxoanthryl ring the mode of cyclisation of the benzylic radical (8) [or carbonium ion (11)] has a crucial effect on product distribution. Product analysis is not sufficiently complete in all cases for an exact measure to be made of the extent of each mode of cyclisation and hence for the governing factors to be fully determined. However, the ease of oxidation of the benzylic radicals (8) to the carbonium ions (11) and the conformational preference of the adjacent benziminoyl and reactive carbon centres in (8) and/or (11) are clearly important. Interestingly, from the iminyl (2; Ar = *o*-MeC_6H_4, R = Me) which could not give oxoanthryl-type products the corresponding bibenzyl was obtained in 21% yield. From the large amount of blue intractable material produced in this oxidation we surmise that 3-methylisoindolenines are not stable under the conditions of the persulphate oxidation.

Intramolecular hydrogen abstraction does not occur with mesityl(phenyl)iminyl (3; Ar = 2,4,6-$Me_3C_6H_2$). Oxidation of the acids (1; Ar = 2,4,6-$Me_3C_6H_2$, R = H and Me) gave only the corresponding azine (22%), and starting acid. Steric interaction between one of the *o*-methyls and the adjacent phenyl group must prevent the formation of the near planar transition state necessary for hydrogen transfer to proceed. Similarly, for *o*-methoxyphenyl(phenyl)iminyl (3; Ar = *o*-$MeOC_6H_4$) dimerisation to azine is favoured over hydrogen abstraction *via* a seven-membered transition state, and for t-butyl-(*o*-tolyl)iminyl fragmentation to *o*-toluonitrile occurs in preference to hydrogen abstraction. As phenols are readily oxidised by persulphate, intramolecular hydrogen abstraction by a diaryliminyl from a phenolic hydroxy group could not be examined by the persulphate method (*cf.* ref. 3) and oxidation of *o*-hydroxydiphenylmethyleneamino-oxyacetic acid gave no useful result.

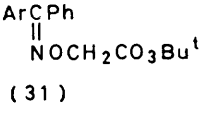
(2) *Decomposition of Imino-oxyperacetates.*—The series of peresters (31; Ar = *o*-MeC_6H_4, *o*-EtC_6H_4, *o*-$Pr^iC_6H_4$, and *o*-$PhCH_2C_6H_4$) was decomposed in benzene as previously described.[4] Many fewer oxoanthryl and isoindoleninyl products were obtained than from the corresponding oxidations with persulphate. The acetals (32) were main products in all cases and for the *o*-methyl- and *o*-ethyl homologues (31; Ar = *o*-MeC_6H_4 and *o*-EtC_6H_4) substantial amounts of the parent ketones were also obtained (Table 2). The imine (5; Ar = *o*-MeC_6H_4) as well as its hydrolysis product, the ketone (6; Ar = *o*-MeC_6H_4), were isolated from the decomposition of the perester (31; Ar = *o*-MeC_6H_4) and although the corresponding imine was not isolated from the perester (31; Ar = *o*-EtC_6H_4) the yield of ketone increased from 11 to 28% when the reaction mixture was left for seven days before work-up. The blue pigment (13) was visibly present in the mixture after thermolysis of the perester (31; Ar = *o*-MeC_6H_4) but was not isolated and this is our only evidence for cyclisation of benzyl radicals and/or cations to isoindolenines in this series of reactions. Cyclisation to an oxoanthryl product did occur (i) on decomposition of the perester (31; Ar = *o*-$Pr^iC_6H_4$) but the yield of 10,10-dimethylanthrone was much lower than from the corresponding persulphate oxidation and (ii) with the *o*-benzyl perester (31; Ar = *o*-$PhCH_2C_6H_4$) leading to formation of the two coloured products mentioned in Section 1.

TABLE 2

Yields (%) of products from peresters (31)

Substrate	Acetal (32)	Ketone (6)	Imine (5)	Azine	Others
(31; Ar = *o*-MeC_6H_4)	22	12	16	†	† (13)
(31; Ar = *o*-$MeOC_6H_4$)	31	31		13	
(31; Ar = 2,4,6-$Me_3C_6H_2$)	31 + 13 *		24	12	
(31; Ar = *o*-EtC_6H_4)	25	28			
(31; Ar = *o*-$PhCH_2C_6H_4$)	25				16 (24) 4 (29) 6 ‡
(31; Ar = *o*-$Pr^iC_6H_4$)	8				19 §

* Stereoisomeric acetals. † Detected by t.l.c. but not isolated. ‡ *o*-Dibenzoylbenzene. § 10,10-Dimethylanthrone.



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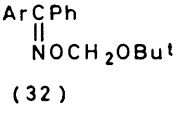

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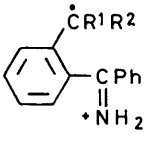

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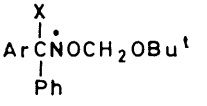

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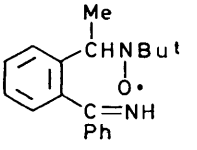

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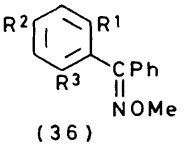

(36)

The orange one, $C_{40}H_{27}NO$ (mass spectrum), $\nu_{max.}$ 1 665 cm^{-1}, is the imine (29) since it was readily hydrolysed in aqueous ethanolic acid to the 9-anthrylamine

(30) (isolated as its picrate) and *o*-benzoylbenzophenone. The yellow one, $C_{40}H_{27}N$, slowly transformed into the imine (29; R^3 = H) on exposure to air, a change which was accelerated when oxygen was bubbled through the solution. U.v. irradiation of its solution in aqueous butanol saturated with oxygen gave the imine (29) in quantitative yield. These observations, and the similarity of its u.v. spectrum to that of 1,2,3-triphenylisoindole [12,13] lead us to the isoindole structure (24). Thus, we assume that like 1,2,3-triphenylisoindole,[13] the isoindole (24) reacts with oxygen to give an *endo*-peroxide (27) which is converted into the imine (29) *via* the biradical (28) (*cf.* ref. 14). Similar treatment of the *endo*-peroxide of 1,2,3-triphenylisoindole [13,15] gives *o*-benzoylbenzophenone and aniline rather than the imine corresponding to (29). Indeed, the *N*-anthrylimine (29) seems to be significantly more resistant to hydrolysis than its *N*-phenyl analogues.[13,14] We attribute this difference to non-bonding interactions between the *o*-benzoyl and anthryl groups in (29) which cause the *o*-benzoyl group to be twisted out of conjugation with the ring to some extent and/or to electron donation by the phenylanthryl group as indicated in (29a). Accordingly, nucleophilic addition of water at the imino carbon (29) is less favourable than at the corresponding imino carbon of the imine derived from 1,2,3-triphenylisoindole and some of the imine (29) survives even under the conditions of the persulphate oxidation. Formation of the isoindole (24) probably involves coupling of benzyl (8) and oxoanthrylimine (15) radicals (on nitrogen) followed by internal condensation with loss of ammonia as indicated in Scheme 3.

Decomposition of the *o*-methoxyphenyl and mesityl peresters (31; Ar = *o*-$MeOC_6H_4$ and 2,4,6-$Me_3C_6H_2$) gave products similar to those obtained from the corresponding persulphate oxidations but the yields of azine were lower (Table 2). Interestingly, no ketone was isolated from the mesityl perester (31; Ar = 2,4,6-$Me_3C_6H_2$), only the imine (5; Ar = 2,4,6-$Me_3C_6H_2$). This imine is particularly resistant to hydrolysis and so this result provides further evidence that yields of ketones are equivalent to imines, and hence measure the extent of intermolecular hydrogen abstraction.

Comparison of the products obtained by thermolysis of the peresters in benzene and by aqueous persulphate oxidation of the corresponding imino-oxyacetic acids reveals a significant difference in the reactivity of the iminyls so generated. When the iminyls are generated by the former method intermolecular prevails over intramolecular hydrogen abstraction resulting in increased yields of ketones (or imines) and reduced yields of oxoanthryl and isoindoleninyl products. A similar difference became apparent in related work with alkyl(aryl)iminyls whose reactions were more suitable for close scrutiny than those of the *o*-alkyldiarylaminyls described herein. This investigation is described fully in Part 5 but it is appropriate here to apply its findings to the present results. Iminyls generated by the persulphate method are in equilibrium with their iminium radical-cations [reaction (1)] in the aqueous acidic reaction mixture. The iminium radical ions are better hydrogen abstractors than the iminyls and hence 1,6 hydrogen transfer to produce benzylic radicals (33) is more efficient in the persulphate oxidations than in the perester decompositions. This leads to the observed increase in yields of oxoanthryl and isoindoleninyl products (Section 1). Significantly, the peresters which give the highest yields of oxoanthryl-type products, *viz.* (31; Ar = *o*-$PhCH_2C_6H_4$ and *o*-$Pr^iC_6H_4$), are those which have the most easily abstracted benzylic hydrogens, *i.e.*, hydrogens which may be abstracted by the less reactive neutral iminyls.

$$Ar_2C{=}N\cdot + H^+ \rightleftharpoons Ar_2C{=}\overset{+\cdot}{N}H \qquad (1)$$

TABLE 3

Hyperfine coupling constants (G) of radicals generated from t-butyl peresters (31)

Perester	Conditions	*g* Value	Coupling constant	Assignment
(31; Ar = *o*-C_6H_4)	C_6H_6–75°	2.0034	a_N 10.1, a_H 0.3	ArPhC=N·
(31; Ar = *o*-$MeOC_6H_4$)	C_6H_6–75°	2.0034	a_N 10.25, a_H 0.3	ArPhC=N·
(31; Ar = 2,4,6-$Me_3C_6H_2$)	C_6H_6–75°	2.0034	a_N 10.0, a_H 0.25	ArPhC=N·
(31; Ar = *o*-$Pr^iC_6H_4$)	C_6H_6–75°	2.0054	a_N 14.1, a_H 2.0 (2 H)	ArCXPhNOCHOBu^t
(31; Ar = *o*-$PhCH_2C_6H_4$)	C_6H_6–75°	(a) 2.0053	a_N 13.8, a_H 2.2 (2 H)	ArCXPhNOCHOBu^t
		(b) 2.0036	*a* 3.15	(15)
(31; Ar = Ph)	C_6H_6–75°–Bu^{t}NO		a_N 15.4	Bu$^t{}_2$NO·
			a_N 27.0	Bu^{t}ON(O)Bu^t
(31; Ar = *o*-EtC_6H_4)	C_6H_6–75°–Bu^{t}NO		a_N 15.4	Bu$^t{}_2$NO·
			a_N 27.0	Bu^{t}ON(O)Bu^t
			a_N 14.8, a_H 3.0 (1 H)	(35)

E.s.r. Spectra.—Thermolysis of solutions of the peresters (31; Ar = *o*-MeC_6H_4, *o*-$MeOC_6H_4$, and 2,4,6-$Me_3C_6H_2$) in benzene at 75° in an e.s.r. spectrometer gave spectra of the corresponding iminyls (a_N 10.0 G, *g* 2.003 0) (Table 3). The hyperfine proton splitting (a_H 0.3 G) was not sufficiently well resolved to permit full analyses. Iminyls were not detected on similar treatment of the peresters (31; Ar = *o*-EtC_6H_4, *o*-$Pr^iC_6H_4$, and *o*-$PhCH_2C_6H_4$), and of t-butyl 1-*o*-methylphenylethylideneamino-oxyperacetate. The *o*-isopropyl and *o*-benzyl peresters gave spectra which we attribute to the alkoxyaminyls (34; Ar = *o*-$Pr^iC_6H_4$ and *o*-PhC_6H_4) formed by addition of an unknown radical (X·) to the corresponding acetal. The latter spectrum faded slowly and was replaced by a longer-lived one which, although not fully resolved, is possibly due to the oxoanthryl (15; O in place of NH) (*cf.* refs. 16 and 17) (Table 2). Photolysis of the peresters and of the oxime methyl ethers

(36; R^1 = Me, R^2 = R^3 = H, R^1 = R^2 = R^3 = Me; R^1 = R^2 = Me, R^3 = H) in di-t-butyl peroxide under a variety of conditions failed to produce spectra of either the corresponding iminyls (3) or benzyl radicals (8). However, photolysis of the acetal (32; Ar = *o*-EtC_6H_4) in benzene gave a weak spectrum (a_N 14.6 G, a_H unresolved, *g* 2.005 3) attributable to an alkoxyaminyl of type (34; Ar = *o*-EtC_6H_4).

Iminyls cannot be trapped by reaction with 2-methyl-2-nitrosopropane. Thus, when the perester (31; Ar = Ph) was warmed in benzene with the nitroso trap only di-t-butyl and t-butyl t-butoxy nitroxides were detected. However, with the *o*-methyl, *o*-ethyl, and *o*-benzyl peresters complex spectra arising from several nitroxides were detected. Presumably, these arise by trapping of the several secondary carbon radicals which are produced in these decompositions. Only with the *o*-ethyl perester did one nitroxide predominate. This was a t-alkyl s-alkyl nitroxide and could be due to the radical (35).

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°. Merck GF_{254} silica was used for chromatographic separations.

Preparation of Ketones, Imines, and Oximes.—Apart from *o*-isopropylbenzophenone [18] ketones were prepared from the appropriate aryl or alkyl Grignard reagent and arenecarbonitrile.[19] The following are known compounds: *o*-methyl-,[20] *o*-ethyl-,[21] *o*-benzyl,[22] *o*-methoxy-,[23] and 2,4-dimethyl- [24] benzophenones, *o*-methylacetophenone,[25] and phenyl t-butyl ketone.[26] *o*-Methoxymethoxybenzophenone could not be prepared as described by Henecka.[27] Instead chlorodimethyl ether (30 g) was added dropwise to a vigorously stirred mixture of *o*-hydroxybenzophenone (30 g, 0.15 mol) and anhydrous potassium carbonate (100 g) in acetone (800 ml) under reflux. After 1 h the mixture was filtered, and the residue was washed with acetone. The combined filtrates were evaporated to dryness, and the residue was dissolved in ether. *o*-Hydroxybenzophenone was removed from the ethereal solution by exhaustive extraction with 2M-sodium hydroxide solution. The ethereal solution was washed with water, dried, and evaporated to give the product as an oil (29 g, 80%), $\nu_{max.}$ (film) 1 667 cm^{-1}, δ 3.27 (3 H, s, OMe), 4.99 (2 H, s, OCH_2O), and 7.00—7.90 (9 H, m, ArH). 2,4,6-Trimethylbenzophenone imine was obtained from its hydrochloride, m.p. 269—273° (lit.,[28] 255—260°) which was formed by reaction of mesitylmagnesium bromide with benzonitrile followed by hydrolysis with dilute hydrochloric acid. Treatment of the hydrochloride with aqueous base followed by extraction of the mixture with ether gave, after removal of solvent and distillation of the residual oil, *2,4,6-trimethylbenzophenone imine* as a liquid, b.p. 140—142° at 0.4 mmHg (Found: C, 86.8; H, 7.6; N, 6.1. $C_{16}H_{17}N$ requires C, 86.05; H, 7.65; N, 6.25%), $\nu_{max.}$ 3 245 and 3 210 cm^{-1}, δ 2.02 (6 H, s, 2Me), 2.23 (3 H, s, Me), and 9.38 (1 H, s, NH).

Oximes were prepared by heating the ketone or imine hydrochloride (0.1 mol) and hydroxylamine hydrochloride (0.22 mol) with potassium hydroxide (0.5 mol) [or sodium acetate with 2,4,6-trimethylbenzophenone] in aqueous alcoholic solution under reflux for 1—16 h. The following are new: *o-ethylbenzophenone oxime*, needles, m.p. 87—90° (from aqueous methanol) (Found: C, 80.2; H, 6.8; N, 6.1. $C_{15}H_{15}NO$ requires C, 79.75; H, 6.7; N, 6.2%); *o-benzylbenzophenone oxime*, rhombs, m.p. 145—146° (from methanol) (Found: C, 83.7; H, 6.0; N, 4.6. $C_{20}H_{17}NO$ requires C, 83.6; H, 5.95; N, 4.85%); *o-isopropylbenzophenone*, rhombs, m.p. 107—115° (from pentane) (Found: C, 80.4; H, 7.4; N, 6.0. $C_{16}H_{17}NO$ requires C, 80.3; H, 7.15; N, 5.85%); *o-methoxymethoxybenzophenone oxime*, rhombs, m.p. 69—75° (from chloroform–hexane) (Found: C, 69.9; H, 5.8; N, 5.5. $C_{15}H_{15}NO_3$ requires C, 70.0; H, 5.9; N, 5.45%), δ (mixture of *syn*- and *anti*-isomers, ratio 3 : 7) 3.12 and 3.24 (total 3 H, each s, *anti*- and *syn*-MeO), 4.90 and 5.04 (total 2 H, each s, *anti*- and *syn*-OCH_2O), and 6.9—7.7 (9 H, m, ArH).

Preparation of Imino-oxyacetic Acids.—These were prepared as previously described.[1] The following are new: *o-methyldiphenylmethyleneamino-oxyacetic acid*, plates, m.p. 145—147° (from aqueous alcohol) (Found: C, 71.1; H, 5.7; N, 5.1. $C_{16}H_{15}NO_3$ requires C, 71.4; H, 5.6; N, 5.2%), $\nu_{max.}$ 1 726 cm^{-1}, δ 2.17 (3 H, s, Me) and 4.64 (2 H, s, OCH_2); *2,4-dimethyldiphenylmethyleneamino-oxyacetic acid*, needles, m.p. 123—128° (from chloroform–petrol) (Found: C, 71.8; H, 5.9; N, 4.8. $C_{17}H_{17}NO_3$ requires C, 72.05; H, 6.05; N, 4.95%), $\nu_{max.}$ 1 731 and 1 715 cm^{-1}, δ 2.17 (3 H, s, Me), 2.38 (3 H, s, Me), and 4.70 (2 H, s, OCH_2); *2,4,6-trimethyldiphenylmethyleneamino-oxyacetic acid*, needles, m.p. 159—160° (from petrol) (Found: C, 72.5; H, 6.7; N, 4.9. $C_{18}H_{19}NO_3$ requires C, 72.7; H, 6.45; N, 4.7%), $\nu_{max.}$ 1 730 and 1 712 cm^{-1}, δ 2.12 (6 H, s, 2Me), 2.32 (3 H, s, Me), and 4.70 (2 H, s, OCH_2); *o-ethyldiphenylmethyleneamino-oxyacetic acid*, rhombs, m.p. 127—130.5° (from aqueous alcohol) (Found: C, 72.1; H, 6.0; N, 4.8. $C_{17}H_{17}NO_3$ requires C, 72.05; H, 6.05; N, 4.95%), $\nu_{max.}$ 1 730 cm^{-1}, δ 1.10 (3 H, t, *J* 7.5 Hz, CH_2), 2.54 (2 H, q, *J* 7.5 Hz, CH_2), and 4.72 (2 H, s, OCH_2); *o-benzyldiphenylmethyleneamino-oxyacetic acid*, needles, m.p. 119—123° (from aqueous methanol) (Found: C, 76.4; H, 5.7; N, 4.0. $C_{22}H_{19}NO_3$ requires C, 76.5; H, 5.55; N, 4.05%), $\nu_{max.}$ 1 728 cm^{-1}, δ 3.87 (2 H, s, CH_2Ph) and 4.59 (2 H, s, OCH_2); *o*-methoxydiphenylmethyleneamino-oxyacetic acid gave two isomers separable by fractional crystallisation from ethanol; the more soluble isomer (i) gave plates, m.p. 122—127° (from water) (Found: C, 67.3; H, 5.0; N, 5.2. Calc. for $C_{16}H_{15}NO_4$: C, 67.35; H, 5.3; N, 4.9%), $\nu_{max.}$ 1 735 and 1 701 cm^{-1}, δ 3.63 (3 H, s, MeO) and 4.75 (2 H, s, OCH_2); the less soluble isomer (ii) gave plates, m.p. 142—144° (from aqueous methanol) (Found: C, 67.0; H, 5.4; N, 5.2. $C_{16}H_{15}NO_4$ requires C, 67.35; H, 5.3; N, 4.9%), $\nu_{max.}$ 1 719 cm^{-1}, δ 3.87 (3 H, s, OMe) and 4.75 (2 H, s, OCH_2); *o-methoxymethoxydiphenylmethyleneamino-oxyacetic acid*, needles, m.p. 89—100° (from chloroform–petrol) (Found: C, 64.6; H, 5.2; N, 4.2. $C_{17}H_{17}NO_5$ requires C, 64.75; H, 5.45; N, 4.45%), $\nu_{max.}$ 1 725 cm^{-1}, δ (mixture of *syn*- and *anti*-acids in the ratio 27 : 73) 3.13 and 3.30 (total 3 H, each s, *syn*- and *anti*-MeO), 4.75 (total 2 H, s, *syn*- and *anti*-CH_2CO_2H), 4.91 and 5.15 (total 2 H, each s, *syn*- and *anti*-OCH_2O) [hydrolysis of this product with M aqueous sulphuric acid in glacial acetic acid under reflux for 1 min gave *o-hydroxydiphenylmethyleneamino-oxyacetic acid*, needles, m.p. 139—143° (from aqueous acetic acid) (Found: C, 66.4; H, 4.8; N, 5.0. $C_{15}H_{13}NO_4$ requires C, 66.4; H, 4.85; N, 5.15%), $\nu_{max.}$ 3 460 and 1 719 cm^{-1}, δ 4.66 (2 H, s, OCH_2), 6.6—7.6 (9 H, m, ArH), and 9.1br (2 H, s, 20H)];

o-*isopropyldiphenylmethyleneamino-oxyacetic acid*, prisms, m.p. 146—148° (from chloroform–petrol) (Found: C, 72.8; H, 6.7; N, 5.0. $C_{18}H_{19}NO_3$ requires C, 72.7; H, 6.35; N, 4.7%), $\nu_{max.}$ 1 733 and 1 716 cm^{-1}, δ (mixture of isomers in the ratio 44 : 56) 1.03 and 1.07 (total 6 H, each d, *J* 7 Hz, Me_2CH), *ca.* 2.92 (total 1 H, each septet, *J* 7 Hz, $CHMe_2$), 4.69 and 4.76 (total 2 H, each s, OCH_2), 7.0—7.8 (9 H, m, ArH), and 10.70br (1 H, each s, CO_2H); 1-o-*methylphenylethylideneamino-oxyacetic acid*, liquid, b.p. 167—169° at 0.7 mmHg (Found: C, 63.9; H, 6.5; N, 6.5. $C_{11}H_{13}NO_3$ requires C, 63.75; H, 6.3; N, 6.75%), $\nu_{max.}$ 1 739 cm^{-1}, δ 2.24 (3 H, s, CH_3), 2.33 (3 H, s, ArMe), and 4.71 (2 H, s, OCH_2); (2,2-*dimethyl*-1-o-*methylphenylpropylidene*)*amino-oxyacetic acid*, needles, m.p. 113—115° (from aqueous alcohol) (Found: C, 67.5; H, 7.7; N, 5.9. $C_{14}H_{19}NO_3$ requires C, 67.45; H, 7.7; N, 5.6%), $\nu_{max.}$ 1 728 and 1 709 cm^{-1}, δ 1.18 (9 H, s, Bu^t), 2.27 (3 H, s, ArMe), and 4.53 (2 H, s, OCH_2).

Preparation of 2-Imino-oxy-2-methylpropanoic Acids.—These were prepared following the method of Corey *et al.*:[29] 2-(o-*methyldiphenylmethylamino-oxy*-2-*methylpropanoic acid* gave plates, m.p. 131—135° (from petrol) (Found: C, 72.5; H, 6.7; N, 4.9. $C_{18}H_{19}NO_3$ requires C, 72.7; H, 6.45; N, 4.7%), $\nu_{max.}$ 1 723 and 1 703 cm^{-1}, δ 1.50 (6 H, s, Me_2C), 2.17 (3 H, s, ArMe), and 9.88br (1 H, s, OH); 2-(2,4-*dimethyldiphenylmethyleneamino-oxy*)-2-*methylpropanoic acid*, plates, m.p. 140—141° (from petrol) (Found: C, 73.0; H, 6.8; N, 4.3. $C_{19}H_{21}NO_3$ requires C, 73.3; H, 6.8; N, 4.5%), $\nu_{max.}$ 1 706 cm^{-1}, δ 1.53 (6 H, s, Me_2C), 2.14 (3 H, s, Me), 2.35 (3 H, s, Me), and 10.77br (1 H, s, OH); 2-*methyl*-2-(2,4,6-*trimethyldiphenylmethyleneamino-oxy*)*propanoic acid*, rhombs, m.p. 164—164.5° (Found: C, 73.7; H, 7.4; N, 4.2. $C_{20}H_{23}NO_3$ requires C, 73.8; H, 7.1; N, 4.3%), $\nu_{max.}$ 1 702 and 1 723 cm^{-1}, δ 1.53 (6 H, s, Me_2C), 2.07 (6 H, s, 2ArMe), 2.33 (3 H, s, ArMe), and 10.68br (1 H, s, OH).

Oxidation of Imino-oxyacetic Acids with Persulphate.—These were carried out as described previously.[1,4]

o-Methyldiphenylmethyleneamino-oxyacetic acid (3.23 g) gave a blue neutral residue, chromatography (column) of which yielded, in order of decreasing R_F, (i) 3-phenyl-1-[(3-phenyl-2*H*-isoindol-1-yl)methylene]-1*H*-isoindole (13; R^3 = H) (34 mg, 1.5%) as deep blue needles, m.p. 244—246° (lit.,[7] 245°) (from acetone) (Found: M^+, 396.162 8. Calc. for $C_{29}H_{20}N_2$: *M*, 396.162 6), $\lambda_{max.}$ (benzene) 295, 307, 341sh, and 595 nm (log ε 4.37, 4.36, 4.20, and 4.62), $\lambda_{max.}$ (dioxan) 591 nm (log ε 4.53); gentle warming of the blue pigment (8 mg) with acetic anhydride (0.2 ml) containing a trace of concentrated sulphuric acid gave the *acetyl derivative* (9.6 mg), long green needles, m.p. 254—257° (from acetic anhydride) (Found: C, 84.9; H, 4.8%; M^+, 438.173 2. $C_{31}H_{22}N_2O$ requires C, 84.9; H, 5.05%; *M*, 438.173 2), $\nu_{max.}$ 1 742 and 1 711 cm^{-1}; (ii) o-*methylbenzophenone azine* (12 mg, 1.0%), green-yellow needles, m.p. 137—142° (from methanol) identical with an authentic specimen; (iii) o-methylbenzophenone (490 mg, 23%); (iv) anthraquinone (576 mg, 23%) identical with an authentic specimen; (v) 1-*phenyl*-3,4-*dihydroisoquinoline*-3-*spiro*-10′-*anthrone* (25; R^1 = R^2 = R^3 = H) (100 mg, 4.3%), rhombs, m.p. 178° (from methanol or acetone) [Found: C, 87.3; H, 5.2; N, 3.8%; M^+, 385.146 3; *M* (osmometric), 381. $C_{28}H_{19}NO$ requires C, 87.25; H, 4.95; N, 3.65%; *M*, 385.146 6], $\nu_{max.}$ 3 070, 3 015, 2 930, and 1 669 cm^{-1}, δ 3.18 (2 H, s, CH_2), 6.84 (1 H, m, ArH), 7.20—7.60 (12 H, m, ArH), 7.82 (2 H, m, o-H of 1-Ph), 8.26 (2 H, m, 1′,8′-ArH), δ_C 47.31 (CH), 61.87 (3-C), 146.5 (C=N), and 169.0 (C=O); and (vi) 2,2′-dibenzoylbibenzyl (123 mg, 5.2%), m.p. 108—110° (lit.,[30] 109—110°), $\nu_{max.}$ 1 658 cm^{-1}, δ 2.94 (4 H, s, $2CH_2$) and 7.19—7.85 (18 H, m, ArH).

When the oxidation was repeated with (a) addition of copper(II) sulphate (1 mol) to the acid before treatment with persulphate, (b) simultaneous addition of a solution of copper(II) sulphate (1 mol) and the persulphate solution to the acid, and (c) addition of persulphate to a suspension of the copper(II) salt of the acid, the following products were formed in each case: (i) o-methylbenzophenone (29%); (ii) 3,3′-diphenylbi-1*H*-isoindol-1-ylidene (19; R^3 = H) (8%) as orange needles, m.p. 260—262° (lit.,[10] 259—260°) (from benzene) (Found: C, 87.7; H, 5.0; N, 7.2%; M^+, 382.146 7. Calc. for $C_{28}H_{18}N_2$: C, 87.95; H, 4.75; N, 7.3%; *M*, 382.146 9), $\lambda_{max.}$ (benzene) 456 nm (log ε 4.48), δ 7.45—8.02 (12 H, m, ArH), 8.32 (4 H, m, o-H of Ph), and 9.09 (2 H, m, 4- and 4′-ArH); (iii) 10-(3-*phenyl*-1H-*isoindol*-1-*ylidene*)*anthrone* (18; R^3 = H) (6%), yellow rhombs, m.p. 208—210° (from petrol) (Found: C, 87.5; H, 4.3; N, 3.8%; M^+, 383. $C_{28}H_{17}NO$ requires C, 87.7; H, 4.45; N, 3.65%; *M*, 383), $\lambda_{max.}$ (benzene) 434 nm (log ε 4.20), $\nu_{max.}$ 1 667 cm^{-1}, δ 7.10—7.90 (11 H, m, ArH), 8.20 (5 H, m, o-H of Ph, 1- and 8-ArH and one other ArH), and 9.34 (1 H, m, 4-ArH); (iv) anthraquinone, the bibenzyl (9; R^1 = R^2 = R^3 = H), and spiro compound (25; R^1 = R^2 = R^3 = H) present in lower yield than in previous oxidation (t.l.c.) but not isolated.

2-(o-Methyldiphenylmethyleneamino-oxy)-2-methylpropanoic acid gave the same distribution of products as that obtained from the corresponding imino-oxyacetic acid (t.l.c.) except that blue pigment (13; R^3 = H) was absent.

2,4-Dimethyldiphenylmethyleneamino-oxyacetic acid (300 mg) gave (i) 3-*phenyl*-6-*methyl*-1-[(3-*phenyl*-6-*methyl*-2H-*isoindol*-1-*yl*)*methylene*]-1H-*isoindole* (13; R^3 = Me) (3 mg, 1.3%) as blue needles, m.p. 254—259° (from acetone) (Found: M^+, 424.193 8. $C_{31}H_{24}N_2$ requires *M*, 424.193 9), $\nu_{max.}$ (chloroform) 2 920, 2 855, and 1 614 cm^{-1}; (ii) 2,4-dimethylbenzophenone azine (1 mg, 0.5%), yellow needles, m.p. 134—139° (lit.,[31] 137—139.5°) (from methanol) identical with an authentic sample; (iii) 2,4-dimethylbenzophenone (16%); (iv) 2-methylanthraquinone (26 mg, 11%), m.p. 175—179° (lit.,[32] 177—179°) identical with authentic material, $\nu_{max.}$ 1 675 cm^{-1}, δ 2.51 (3 H, s, Me); (v) 3,4-*dihydro*-1-*phenyl*-3′,6-*dimethylisoquinoline*-3-*spiro*-10′-*anthrone* (25; R^1 = R^2 = H, R^3 = Me) (19 mg, 9%), rhombs, m.p. 212—214° (from methanol) (Found: C, 87.0; H, 5.7; N, 3.4%; M^+, 413.176 9. $C_{30}H_{23}NO$ requires C, 87.15; H, 5.6; H, 3.4%; *M*, 413.177 9), $\nu_{max.}$ 3 060, 3 015, 2 920, and 1 664 cm^{-1}, δ 2.32 (6 H, m, 2Me), 3.16 (2 H, m, CH_2), 6.68 (1 H, s, ArH), 7.02—7.58 (10 H, m, ArH), 7.82 (2 H, m, o-H of Ph), and 8.22 (2 H, m, 1′,8′-ArH); (vi) 2,2′-*dibenzoyl*-5,5′-*dimethylbibenzyl* (6 mg, 3%), needles, m.p. 145—148° (from ethanol) (Found: C, 86.0; H, 6.5. $C_{30}H_{26}O_3$ requires C, 86.1; H, 6.25%), $\nu_{max.}$ 1 662 cm^{-1}, δ 2.30 (6 H, s, 2Me), 2.94 (4 H, s, CH_2CH_2), and 6.90—7.82 (16 H, m, ArH).

2-(2,4-Dimethyldiphenylmethyleneamino-oxy)-2-methylpropanoic acid (4.4 g) gave (i) the azine (4; Ar = 2,4-$Me_2C_6H_3$) (trace); (ii) 2,4-dimethylbenzophenone (582 mg, 20%); (iii) 2-methylanthraquinone (94 mg, 3%); (iv) the bibenzyl (9; R^1 = R^2 = H, R^3 = Me) (160 mg, 5.3%); (v) the spiro compound (25; R^1 = R^2 = H, R^3 = Me) (102 mg, 3.5%).

2,4,6-Trimethyldiphenylmethyleneamino-oxyacetic acid (594 mg) gave 2,4,6-*trimethylbenzophenone azine* (56 mg, 22%) as yellow needles, m.p. 223—226° (from ethanol) (Found: C, 86.4; H, 7.4; N, 6.5%; M^+, 444.256 8. $C_{32}H_{32}N_2$ requires C, 86.45; H, 7.25; N, 6.3%; *M*, 444.256 5), δ 2.06 (12 H, s, *o*-Me), 2.38 (6 H, s, *p*-Me), 6.93 (4 H, s, *m*-H or $Me_3C_6H_2$), and 7.29 (10 H, m, ArHO, and unchanged acid (210 mg).

2-Methyl-2-(2,4,6-trimethyldiphenylmethyleneamino-oxy)propanoic acid (325 mg) gave the azine (4; Ar = 2,4,6-$Me_3C_6H_2$) (30 mg) (20%), and unchanged acid (100 mg).

o-Methoxydiphenylmethyleneamino-oxyacetic acid (570 mg) gave o-*methoxybenzophenone azine* (370 mg, 88%) as yellow prisms, m.p. 187—189° (from benzene) (Found: C, 80.2; H, 5.7; N, 6.7. $C_{28}H_{24}N_2O_2$ requires C, 80.0; H, 5.75; N, 6.65%), δ 3.69 (6 H, s, 2MeO) and 6.88—7.58 (18 H, m, ArH), identical with an authentic specimen.

o-Ethyldiphenylmethyleneamino-oxyacetic acid (1.132 g) gave (i) *o*-ethylbenzophenone (trace); (ii) anthraquinone (5 mg, 1%); (iii) 10-hydroxy-10-methyl-9-anthrone (260 mg, 46%), needles, m.p. 153—154° (lit.,[33] 154°) (from chloroform–petrol) (Found: C, 80.3; H, 5.4. Calc. for $C_{15}H_{12}O_2$: C, 80.35; H, 5.4%), $\nu_{max.}$ 3 430 and 1 650 cm^{-1}, δ 1.66 (3 H, s, Me), 2.75br (1 H, s, OH), and 7.24—8.20 (8 H, m, ArH); and (iv) unchanged acid (432 mg).

o-Benzyldiphenylmethyleneamino-oxyacetic acid (1.38 g) gave (i) 1,3-diphenyl-*N*-(10-phenyl-9-anthryl)isoindole (22; R^1 = Ph, R^3 = H) (16 mg, 2.5%); (ii) 1,3-*diphenyl*-1-(2-*benzoyldiphenylmethyl*)*isoindolenine* (20; R^1 = Ph, R^2 = R^3 = H) (58 mg, 8%), needles, m.p. 188—189° (from benzene–methanol) [Found: C, 89.0; H, 5.4; N, 2.5%; *M* (osmometric), 586. $C_{40}H_{29}NO$ requires C, 89.0; H, 5.4; N, 2.6%; *M*, 539], $\nu_{max.}$ 1 657 cm^{-1}, δ 6.0 (1 H, s, CH), 6.65 (3 H, s, ArH), 6.80—7.90 (23 H, m, ArH), and 8.97 (1 H, d, ArH); (iii) [o-*benzoylphenyl*(*phenyl*)*methylene*]-N-(10-*phenyl*-9-*anthryl*)*amine* (29) (11 mg, 1.5%); (iv) 10-hydroxy-10-phenyl-9-anthrone (245 mg, 35%), rhombs, m.p. 210—212° (lit.,[28] 211—212°) (from chloroform–petrol) (Found: C, 84.1; H, 4.6. Calc. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.95%), $\nu_{max.}$ 3 430 and 1 650 cm^{-1}, δ 3.15 (1 H, s, OH), 7.13—7.64 (11 H, m, ArH), 8.19 (2 H, dd, 1-, 8-ArH); and (v) unchanged acid (430 mg).

1-*o*-Methylphenylethylideneamino-oxyacetic acid (2.07 g) gave a mauve precipitate (1.24 g), chromatography of which gave 2,2′-*diacetylbibenzyl* (281 mg, 21%) as needles, m.p. 150—151° (from ethyl methyl ketone) (Found: C, 81.2; H, 6.7. $C_{18}H_{18}O_2$ requires C, 81.15; H, 6.8%), $\nu_{max.}$ 1 673 cm^{-1}, δ 2.57 (6 H, s, 2Me), 3.15 (4 H, s, CH_2CH_2), and 6.98—7.75 (8 H, m, ArH).

(2,2-Dimethyl-1-*o*-methylphenylpropylidene)amino-oxyacetic acid (1.5 g) gave *o*-toluonitrile (350 mg, 50%, 53.5% by i.r.), an oil identical with an authentic sample.

o-Isopropyldiphenylmethyleneamino-oxyacetic acid (119 mg) gave 10,10-dimethyl-9-anthrone (51 mg, 97%), cream needles, m.p. 96—98° (lit.,[34] 95°) (Found: M^+, 222. Calc. for $C_{16}H_{14}O$: *M*, 222), $\nu_{max.}$ 1 657 cm^{-1}, δ 1.73 (6 H, s, 2Me), 7.25—7.80 (6 H, m, ArH), and 8.40 (2 H, m, ArH, 1- and 8-H), and unchanged acid (49 mg).

Other Oxidations.—*o*-Methyldiphenylmethyleneamino-oxyacetic acid (2.0 mmol) was heated with silver picolinate (2.0 mmol) and pyridine (10 mmol) in benzene to give a complex mixture of products from which only 3,3′-diphenyl-bi-1*H*-isoindolenine (19; R^3 = H) was isolated (5 mg, 1.5%), m.p. 259—260° (lit.,[10] 259—260°) (from petrol) (Found: M^+, 382.146 7. Calc. for $C_{28}H_{19}N_2$: *M*, 382.146 9) $\lambda_{max.}$ (benzene) 456 nm, identical with material described earlier.

o-Methylbenzophenone oxime on oxidation with persulphate gave *o*-methylbenzophenone (trace) and unchanged oxime (>90%).

o-Methylbenzophenone on oxidation with persulphate gave 2,2′-dibenzoylbibenzyl (trace) and unchanged ketone (>90%).

Preparation of Azines.—The following azines were prepared from the ketone (1 mmol) and hydrazone (1 mmol) by heating under reflux in n-butanol for seven days. The three hydrazones are new. o-*Methylbenzophenone hydrazone* gave pale yellow plates, m.p. 114—115.5° (from ethanol) (Found: C, 80.1; H, 6.7; N, 13.0. $C_{14}H_{14}N_2$ requires C, 79.95; H, 6.7; N, 13.3%), $\nu_{max.}$ 3 380, 3 265, and 3 200 cm^{-1}, δ 2.16 (3 H, s, Me) and 5.35br (2 H, s, NH_2); 2,4-*dimethylbenzophenone hydrazone* was an oil (Found: C, 80.5; H, 7.2; N, 12.7. $C_{15}H_{16}N_2$ requires C, 80.3; H, 7.2; N, 12.5%), $\nu_{max.}$ 3 405, 3 285, and 3 200 cm^{-1}, δ 2.10 (3 H, s, Me), 2.35 (3 H, s, Me), and 5.27br (2 H, s, NH_2); o-*methoxybenzophenone hydrazone*, gave plates, m.p. 65—67° (from ethanol) (Found: C, 74.2; N, 5.9; N, 12.7. $C_{14}H_{14}N_2O$ requires C, 74.3; H, 6.25; N, 12.5%), δ 3.73 (3 H, s, OMe), 5.35br (2 H, s, NH_2); o-*methylbenzophenone azine* afforded lime-green rhombs, m.p. 140—143: (from methanol) (Found: C, 86.3; H, 6.4; N, 6.9. $C_{28}H_{24}N_2$ requires C, 86.5; H, 6.25; N, 7.2%); 2,4-dimethylbenzophenone azine, bright yellow needles, m.p. 134—139° (from methanol) (lit.,[25] 137—139°) (Found: C, 86.2; H, 6.4; N, 6.7. Calc. for $C_{30}H_{28}N_2$: C, 86.5; H, 6.8; N, 6.7%); o-*methoxybenzophenone azine*, yellow prisms, m.p. 187—189° (from benzene) (Found: C, 80.2; H, 5.7; N, 6.7. $C_{28}H_{24}N_2O_2$ requires C, 80.0; H, 5.75; N, 6.65%).

Preparation of t-Butyl Peresters of Imino-oxyacetic Acids.—The following were prepared from the corresponding acid chloride and t-butyl hydroperoxide, the acid chlorides being generated in the usual way from the acid and thionyl chloride. o-*Methyldiphenylmethyleneamino-oxyacetyl chloride* gave an oil (Found: C, 66.9; H, 5.1; Cl, 12.4; N, 5.2. $C_{16}H_{14}ClNO_2$ requires C, 66.8; H, 4.9; Cl, 12.35; N, 4.9%), $\nu_{max.}$ 1 815 cm^{-1}, δ 2.20 (3 H, s, Me) and 4.91 (2 H, s, OCH_2); the *t-butyl peracetate* was an oil (Found: C, 70.2; H, 6.7; N, 4.0. $C_{20}H_{23}NO_4$ requires C, 70.35; H, 6.8; N, 4.1%), $\nu_{max.}$ 1 790 cm^{-1}, δ 1.32 (9 H, s, Bu^t), 2.23 (3 H, s, Me), and 4.74 (2 H, s, OCH_2). 2,4,6-*Trimethyldiphenylmethyleneamino-oxyacetyl chloride* gave rosettes, m.p. 80—84° (from pentane) (Found: C, 68.2; H, 5.7; Cl, 11.0; N, 4.7. $C_{18}H_{18}ClNO_2$ requires C, 68.5; H, 5.7; Cl, 11.25; N, 4.45%), $\nu_{max.}$ 1 796 cm^{-1}, δ 2.12 (6 H, s, 2Me), 2.33 (3 H, s, Me), and 4.92 (2 H, s, OCH_2); the *t-butyl peracetate* was a pale yellow oil (Found: M^+, 369.193 9. $C_{22}H_{27}NO_4$ requires *M*, 369.194 0), $\nu_{max.}$ 1 795 and 1 780sh cm^{-1}, δ 1.33 (9 H, s, Bu^t), 2.14 (6 H, s, Me), and 2.35 (3 H, s, Me). o-*Ethyldiphenylmethyleneamino-oxyacetyl chloride* gave a pale yellow oil (Found: C, 67.8; H, 5.1; Cl, 12.1; N, 4.7. $C_{17}H_{16}ClNO_2$ requires C, 67.6; H, 5.3; Cl, 11.8; N, 4.65%), $\nu_{max.}$ 1 815 cm^{-1}, δ 1.09 (3 H, t, *J* 8.1 Hz, CH_3), 2.52 (2 H, q, *J* 8.1 Hz, CH_2), and 4.90 (2 H, s, OCH_2); the *t-butyl peracetate* was a pale yellow oil (Found: C, 71.3; H, 6.9; N, 3.9. $C_{21}H_{25}NO_4$ requires C, 70.95; H, 7.1; N, 3.95%), $\nu_{max.}$ 1 798 and 1 780sh cm^{-1}, δ 1.09 (3 H, t, *J* 7.8 Hz, Me), 1.31 (9 H, s, Bu^t), 2.52 (2 H, q, *J* 7.8 Hz, CH_2), and 4.72 (2 H, s, OCH_2). o-*Benzyldiphenylmethyleneamino-oxyacetyl*

chloride afforded a pale yellow oil (Found: C, 72.7; H, 5.0; Cl, 9.8; N, 3.9. $C_{22}H_{18}ClNO_4$ requires C, 72.55; H, 5.0; Cl, 9.75; N, 3.85%), $\nu_{max.}$ 1 812 cm^{-1}, δ 3.84 (2 H, s, CH_2) and 4.82 (2 H, s, OCH_2); the *t-butyl peracetate* was an oil (Found: C, 75.2; H, 6.6; N, 3.5. $C_{26}H_{27}NO_4$ requires C, 74.8; H, 6.5; N, 3.35%), $\nu_{max.}$ 1 788 cm^{-1}, δ 1.30 (9 H, s, Bu^t), 3.87 (2 H, s, $PhCH_2$), and 4.65 (2 H, s, OCH_2). o-*Methoxydiphenylmethyleneamino-oxyacetyl chloride* gave a pale yellow oil (Found: C, 63.4; H, 4.4; Cl, 11.4; N, 4.6. $C_{11}H_{12}ClNO_2$ requires C, 63.25; H, 4.6; Cl, 11.7; N, 4.6%), $\nu_{max.}$ 1 812 cm^{-1}, δ 3.67 (3 H, s, OMe) and 4.89 (2 H, s, OCH_2); the *t-butyl peracetate* was a pale yellow oil (Found: C, 67.2; H, 6.6; N, 4.2. $C_{20}H_{23}NO_5$ requires C, 67.2; H, 6.5; N, 3.9%), $\nu_{max.}$ 1 790 and 1 775 cm^{-1}, δ 1.33 (9 H, s, Bu^t), 3.71 (3 H, s, OMe), and 4.76 (2 H, s, OCH_2). 1-o-*Methylphenylethylideneamino-oxyacetyl chloride* was an oil (Found: C, 58.8; H, 5.3; Cl, 15.5; N, 6.0. $C_{11}H_{12}ClNO_2$ requires C, 58.55; N, 5.4; Cl, 15.7; N, 6.2%), $\nu_{max.}$ 1 815 cm^{-1}, δ 2.53 (3 H, s, Me), 2.57 (3 H, s, ArMe), and 4.96 (2 H, s, OCH_2); the *t-butyl peracetate* was an oil, $\nu_{max.}$ 1 780 and 1 765 cm^{-1}, δ 1.33 (9 H, s, Bu^t), 2.42 (6 H, s, 2Me), and 4.72 (2 H, s, OCH_2).

t-Butyl o-*isopropyldiphenylmethyleneamino-oxyperacetate*, prepared from the corresponding acid, di-imidazolyl ketone, and t-butyl hydroperoxide as previously described,[4,35] was an oil (Found: C, 70.8; H, 7.1; N, 3.4. $C_{22}H_{27}NO_4$ requires C, 71.5; H, 7.35; N, 3.8%), $\nu_{max.}$ 1 795 cm^{-1}, δ 1.09 (6 H, d, Me_2CH), 1.31 (9 H, s, Bu^t), 2.85 (1 H, m, C*H*Me), and 4.72 (2 H, s, OCH_2).

Preparation of Oxime Methyl Ethers.—These were prepared from the corresponding ketone and methoxyamine hydrochloride in pyridine, or from the imine hydrochloride, methoxyamine hydrochloride, and sodium acetate in aqueous alcohol. o-*Methylbenzophenone* O-*methyloxime* formed plates, m.p. 126—129° (Found: C, 80.2; H, 6.6; N, 5.9. $C_{15}H_{15}NO$ requires C, 79.95; H, 6.7; N, 6.2%), δ 2.18 (3 H, s, ArMe) and 3.95 (3 H, s, OCH_2). 2,4-*Dimethylbenzophenone* O-*methyloxime* was a pale yellow oil (Found: C, 80.5; H, 7.4; N, 6.0. $C_{16}H_{17}NO$ requires C, 80.3; H, 7.15; N, 5.85%), δ 2.16 (3 H, s, ArMe), 2.39 (3 H, s, ArMe), and 3.97 (3 H, s, OMe). 2,4,6-Trimethylbenzophenone *O*-methyloxime gave two isomers. The isomer of higher R_F (silica–chloroform–petrol) gave plates, m.p. 49—51° (from methanol) (Found: C, 80.5; H, 7.6; N, 5.3. Calc. for $C_{17}H_{19}NO$: C, 80.6; H, 7.55; N, 5.55%), δ 2.07 (6 H, s, 2ArMe), 2.33 (3 H, s, ArMe), and 3.95 (3 H, s, OMe), and that of lower R_F gave plates, m.p. 90—92° (from methanol) (Found: C, 80.8; H, 7.6; N, 5.4%), δ 2.18 (6 H, s, 2ArMe), 2.30 (3 H, s, ArMe), and 4.01 (3 H, s, OMe).

Decomposition of t-Butyl Peresters of Imino-oxyacetic Acids.—The peresters were decomposed in benzene as previously described.[4] t-Butyl *o*-methyldiphenylmethyleneamino-oxyperacetate (2 g) gave (i) *o*-methylbenzophenone (131 mg, 12%); (ii) o-*methyldiphenylmethyleneamino-oxy-t-butoxymethane* (383 mg, 22%) as an oil (Found: C, 76.7; H, 7.7; N, 4.6. $C_{19}H_{23}NO_2$ requires C, 76.75; H, 7.8; N, 4.7%), δ 1.19 (9 H, s, Bu^t), 2.15 (3 H, s, Me), 5.33 (2 H, s, OCH_2), and 7.03—7.64 (9 H, m, ArH); (iii) *o*-methylbenzophenone imine (189 mg, 16%) as an oil, $\nu_{max.}$ 3 255, 1 605, and 1 598 cm^{-1}, δ 2.14 (3 H, s, ArMe), 7.24—7.75 (9 H, m, ArH), and 8.30br (1 H, s, NH) which was readily hydrolysed on exposure to air to *o*-methylbenzophenone. T.l.c. examination of the product mixture revealed the presence of the blue isoindole (13) and *o*-methylbenzophenone azine but these were not isolated.

t-Butyl *o*-methoxydiphenylmethyleneamino-oxyperacetate (2.1 g) gave (i) *o*-methoxybenzophenone (386 mg, 31%), (ii) *o*-methoxybenzophenone azine (161 mg, 13%) identical with an authentic specimen, and (iii) o-*methoxydiphenylmethyleneamino-oxy-t-butoxymethane* (570 mg, 31%) as an oil (Found: C, 72.9; H, 7.4; N, 4.4. $C_{19}H_{23}NO_3$ requires C, 72.8; H, 7.4; N, 4.45%), δ 1.19 (9 H, s, Bu^t), 3.70 (3 H, s, OMe), 5.34 (2 H, s, OCH_2), and 6.93—7.52 (9 H, m, ArH).

t-Butyl 2,4,6-trimethyldiphenylmethyleneamino-oxyperacetate (225 mg) gave (i) t-butoxy-2,4,6-trimethyldiphenylmethyleneamino-oxymethane in two isomeric forms: the major isomer (62 mg, 31%) crystallised as fronds, m.p. 48—54° (after distillation) (Found: C, 77.7; H, 8.3; N, 4.0. $C_{21}H_{27}NO_2$ requires C, 77.5; H, 8.35; N, 4.3%), δ 1.19 (9 H, s, Bu^t), 2.07 (6 H, s, 2Me), 2.31 (3 H, s, Me), 5.31 (2 H, s, OCH_2), 6.89 (2 H, s, ArH), and 7.22—7.70 (5 H, m, ArH), and the minor isomer (26 mg, 13%), an oil, δ 1.24 (9 H, s, Bu^t), 2.15 (6 H, s, 2Me), 2.26 (3 H, s, Me), 5.30 (2 H, s, OCH_2), 6.76 (2 H, s, ArH), and 7.11—7.60 (5 H, m, ArH); (ii) 2,4,6-trimethylbenzophenone azine (16 mg, 12%) identical with an authentic specimen; and (iii) 2,4,6-trimethylbenzophenone imine (33 mg, 24%) identical with an authentic specimen.

t-Butyl *o*-ethyldiphenylmethyleneamino-oxyperacetate (2.0 g) gave (i) o-*ethyldiphenylmethyleneamino-oxy-t-butoxymethane* (438 mg, 25%), an oil (Found: C, 77.4; H, 8.4; N, 4.6. $C_{20}H_{25}NO_2$ requires C, 77.15; H, 8.1; N, 4.5%), δ 1.08 (3 H, t, *J* 7.8 Hz, Me), 1.19 (9 H, s, Bu^t), 2.49 (2 H, q, *J* 7.8 Hz, CH_2), 5.34 (2 H, s, OCH_2), and 7.05—7.65 (9 H, m, ArH), and (ii) *o*-ethylbenzophenone (123 mg, 11%). When the crude mixture was exposed to air for seven days before work-up the acetal (32; Ar = *o*-EtC_6H_4) (26%) and *o*-ethylbenzophenone (28%) were isolated.

t-Butyl *o*-benzyldiphenylmethyleneamino-oxyperacetate (1.158 g) gave, after column chromatography of the crude product on silica in the dark using chloroform–petrol (6 : 4) as eluant, (i) o-*benzyldiphenylmethyleneamino-oxy-t-butoxymethane* (240 mg, 25%), an oil (Found: C, 80.2; H, 7.5; N, 4.0. $C_{25}H_{27}NO_2$ requires C, 80.4; H, 7.3; N, 3.75%), δ 1.20 (9 H, s, Bu^t), 3.81 (2 H, s, CH_2Ph), 5.28 (2 H, s, OCH_2), and 7.12—7.55 (14 H, m, ArH); (ii) 1,3-*diphenyl*-N-(10-*phenyl*-9-*anthryl*)*isoindole* (24) (116 mg, 16%) as yellow needles, m.p. 286—288° (from n-butanol) (Found: C, 91.8; H, 5.3; N, 2.8%; M^+, 521.216 0. $C_{40}H_{27}N$ requires C, 92.1; H, 5.2; N, 2.7%; *M*, 521.216 1), $\nu_{max.}$ 1 600 cm^{-1}, $\lambda_{max.}$ (benzene) 366sh, 380, and 400sh nm (log ε 4.23, 4.33, and 4.16), δ 6.90—7.86 (ArH); (iii) 1,2-dibenzoylbenzene (47 mg, 6%) as very pale yellow needles, m.p. 141—143° (lit.,[36] 145—147°) (from methanol) identical (t.l.c., i.r., mass spectra) with an authentic specimen; and (iv) [o-*benzoylphenyl*(*phenyl*)*methylene*]-N-(10-*phenyl*-9-*anthryl*)*amine* (29) (30 mg, 4%), orange needles, m.p. 225—230° (from benzene–petrol) (Found: C, 89.1; H, 5.1; N, 2.9%; M^+, 537.211 1. $C_{40}H_{27}NO$ requires C, 89.35; H, 5.05; N, 2.6%; *M*, 537.211 1), $\lambda_{max.}$ (dioxan) 264, 384sh, 403, and 420sh nm (log ε 4.86, 3.75, 3.92, and 3.90), $\nu_{max.}$ 1 665 cm^{-1}, δ 6.70—8.10 (ArH).

t-Butyl *o*-isopropyldiphenylmethyleneamino-oxyperacetate (90 mg) gave (i) 9,9-dimethyl-10-anthrone (10.2 mg, 19%), and (ii) *o*-isopropyldiphenylmethyleneamino-oxy-t-butoxymethane (7 mg, 8%), δ 1.19 (9 H, s, Bu^t) and 5.31

(2 H, s, OCH_2). These products could not be separated by chromatography. Their identities were established by n.m.r. and yields were calculated from the n.m.r. spectrum of the mixture.

Oxidation of Isoindole (24) (cf. *Ref.* 13).—A solution of the isoindole (40 mg) in n-butanol (6 ml) containing water (4 drops) was irradiated (u.v.) and aerated for 2 h under reflux. Evaporation of the solvent gave the anil (29) in quantitative yield. When oxygen was bubbled through a solution of the isoindole (24) in chloroform over a number of days the anil (29) was formed in quantitative yield.

Hydrolysis of the Anil (29).—The anil (40 mg) was heated under reflux in ethanol (6 ml) containing M-sulphuric acid (6 drops) for 3 h under nitrogen. The solvent was evaporated and the residue was triturated with methanol to give *o*-benzoylbenzophenone (14 mg, 64%), as yellow prisms, m.p. 142—144°, identical (t.l.c., i.r., mass spectra) with a commercial sample. Picric acid (20 mg) was added to the methanol mother liquor and the resulting solution was warmed. The *picrate* of 9-amino-10-phenylanthracene (30) (10 mg, 26%) separated as green-yellow needles, m.p. 253—256° (Found: C, 62.4; H, 3.5; N, 11.3. $C_{26}H_{18}N_4O_7$ requires C, 62.65; H, 3.65; N, 11.25%), identical with product obtained from an authentic specimen of 9-amino-10-phenylanthracene [37] and picric acid.

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