Iminyls. Part 6.[1] Diazo- and Alkoxy-iminyls †

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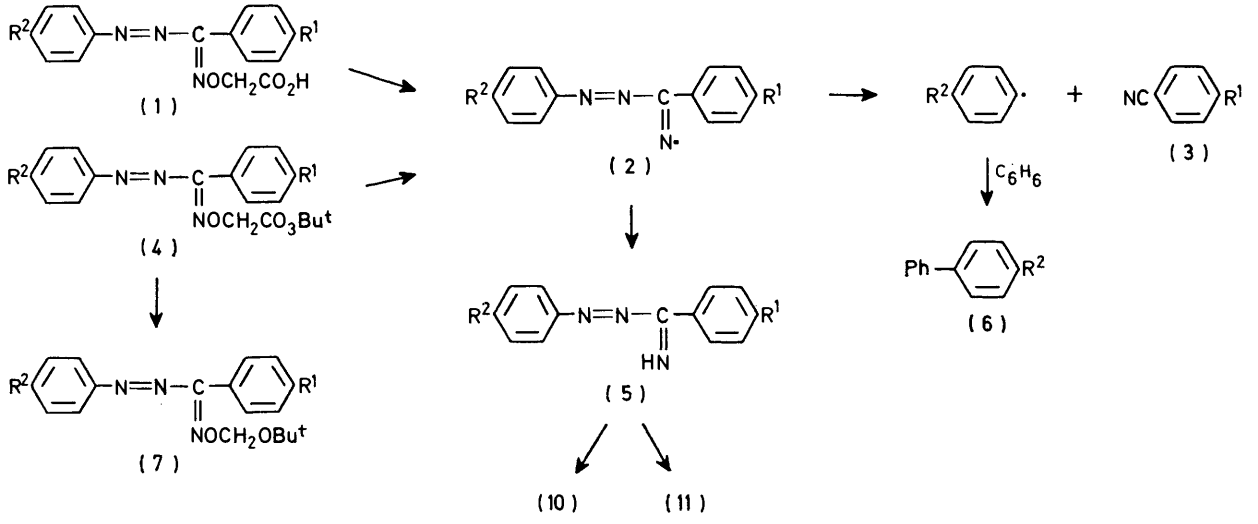
Several diazo- and one alkoxy-aryliminyl(s) have been generated. These (i) fragment to arenecarbonitrile and aryl or alkoxyl radical, respectively, and (ii) abstract hydrogen to give the corresponding imines. The imines derived from the diazoiminyls react further to give triazoles and 2-aroylaminoazoarenes in low yield. Fragmentation of the phenyldiazoiminyls occurs more readily than that of the benzyloxyiminyl and the effect of α-substituents (phenyldiazo, benzyloxy, alkyl) on the ease of fragmentation of phenyliminyls is discussed.

THE methods outlined in Part 1 [2] have been successfully applied in Parts 2—5 to the generation of a variety of iminyls with α-alkyl, hydrogen, and/or aryl substituents. Extension of these procedures to the production of iminyls with α-hetero substituents seemed desirable as such iminyls are not available in other ways and their chemistry is unknown. Accordingly, we have generated several diazoiminyls and one alkoxyiminyl, and examined their reactions.



Diazoiminyls.—Oxidation of the series of arylazoimino-oxyacetic acids (1) listed in Table 1 in the usual way [2] with persulphate in boiling aqueous solution gave the corresponding arenecarbonitrile (3) as the main product (53—70%). Phenylazobenzylideneamino-oxyacetic acid (1; $R^1 = R^2 = H$) also gave two minor products, one orange, the other colourless. The orange one, $C_{19}H_{15}N_3O$ (12%), showed N–H (3 340 cm^{-1}) and carbonyl (1 654 cm^{-1}) absorptions, and was identical with the azo-compound (11; $R^1 = R^2 = H$) produced by condensation of nitrosobenzene with *o*-benzamidoaniline. The colourless product, $C_{14}H_{11}N_3$ (2.5%), whose mass spectrum showed peaks corresponding to sequential loss of HCN and PhCN from the molecular ion, was identified as the triazole (10; $R^1 = R^2 = H$) (Scheme 1) by comparison with a synthetic sample.[3a] The corresponding minor products from the acid (1; $R^1 = Me$, $R^2 = H$) have been identified as the azo-amide (11; $R^1 = Me$, $R^2 = H$) and the triazole (10; $R^1 = Me$, $R^2 = H$). The former, in which the aryl substituents attached to

TABLE 1

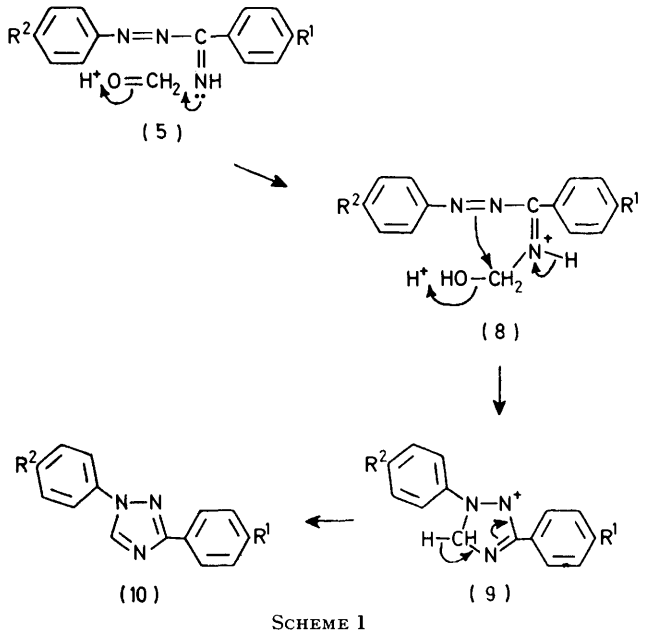
Products (%) from oxidation of Imino-oxyacetic acids (1), (13), and (20) with persulphate

Acid	Nitrile (3)	Triazole (10)	Azo compound (11)	Ketone	Other products
(1; $R^1 = R^2 = H$)	53	2.5	12		
(1; $R^1 = Me$, $R^2 = H$)	60	13	5.5		
(1; $R^1 = H$, $R^2 = Me$)	58	‡			
(1; $R^1 = OMe$, $R^2 = H$)	70				
(13)	7			17 †	17 ($PhCONH_2$)
					21 (PhCHO)
(20; Ar = Ph, R = $PhCH_2$)	67			12	44 ($PhCH_2CH_2Ph$)
(20; Ar = Ph, R = $PhCH_2CH_2$)				30	45 * (22; R = $PhCH_2CH_2$; Ar = Ph)
(20; Ar = *o*-MeC_6H_4, R = Bu^t)	53.5				

* The small amount of 2,4,6-triphenylpyrimidine isolated probably arises from the imine PhCH=CHC(=NH)Ph formed by oxidation of (21; Ar = Ph, R=$PhCH_2CH_2$) or a precursor.[4] † Refers to $PhCO_2CH_2Ph$. ‡ Detected by t.l.c. but not isolated.

† Preliminary communication, A. R. Forrester, M. Gill, E M. Johansson, C. J. Meyer, and R. H. Thomson, *Tetrahedron Letters*, 1977, 3601.

the azo-linkage are both derived from the ArN=N group in the starting acid, and the aroyl group from the ArC=N function, was synthesised from nitrosobenzene



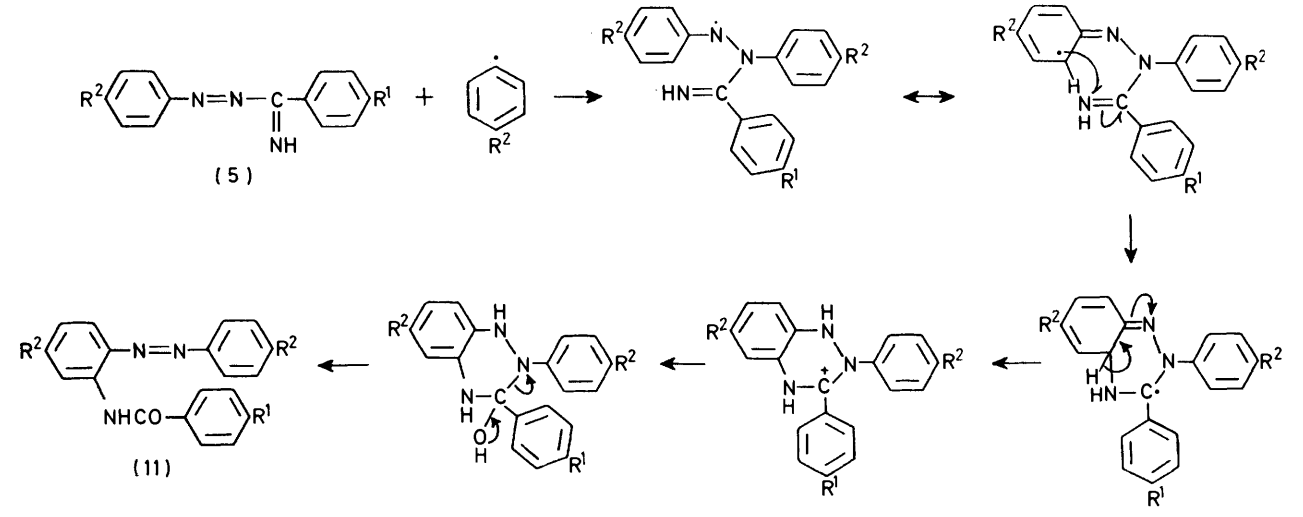
SCHEME 1

and *o*-(*p*-toluamido)aniline. The triazole (10; R^1 = Me, R^2 = H), which shows an unusual highly characteristic [3b] frequency at 3 170 cm^{-1}, fragmented by loss of HCN and C_7H_7CN in the mass spectrometer thus defining the positions of the substituted (C-3) and unsubstituted (N-1) phenyl groups.

The two t-butyl peresters (4; $R^1 = R^2$ = H and R^1 = H, R^2 = Me) also gave the corresponding arenecarbonitrile as the major product on decomposition in hot benzene although the yields were lower than from the corresponding persulphate oxidations. The lower yields we attribute to formation of the acetals (7; $R^1 = R^2$ = H and R^1 = H, R^2 = Me) by cage recombination of the t-butoxyl and imino-oxymethyl radicals thus reducing the efficiency of iminyl formation. The triazoles (10; $R^1 = R^2$ = H and R^1 = H, R^2 = Me) [but not the corresponding aroylaminobenzenes (11)] were also formed on decomposition of the peresters (4; $R^1 = R^2$ = H and R^1 = H, R^2 = Me), respectively, and were accompanied by the biaryls (6; R^2 = H and R^2 = Me). The triazole (10; R^1 = H, R^2 = Me) showed an intense peak (63%) in its mass spectrum corresponding to loss of HCN and PhCN from the molecular ion.

The key intermediates in the above reactions are the diazoiminyls (2) which either fragment (major path) to arenecarbonitrile (3) and aryldiazinyl or abstract hydrogen (minor path) to give the diazoimine (5). The biaryls (6) obtained from the peresters are formed by reaction of aryl radicals (from $ArN_2^{\bullet}$) with solvent. The aryldiazoiminyls (2) are shorter-lived than their styryl analogues,[4] and could not be detected by e.s.r. on decomposition of the peresters (4; $R^1 = R^2$ = H, and R^1 = H, R^2 = Me) in hot benzene. However, with 2-methyl-2-nitrosopropane present the aryl radicals were easily trapped and intense spectra of phenyl and *p*-tolyl t-butyl nitroxides [5] were observed.

C-5 of the triazoles (10) must be derived from the formaldehyde generated on fragmentation of the initial imino-oxymethyl radicals and we envisage triazole formation occurring by reaction of formaldehyde with the imine (5) and subsequent reaction (8) ⟶ (9) ⟶ (10) as outlined in Scheme 1. The origin of the aroylaminobenzenes (11) is less obvious but the exclusive formation of the 2-aroylamino isomer in each case implies intramolecular rearrangement. Addition of an aryl radical to the azoimine (5) to give a hydrazyl seems a likely first step (*cf.* ref. 6), and its subsequent conversion into an aroylaminoazobenzene (11) with the correct arrangement of aryl groups is rationalised in Scheme 2.



SCHEME 2

Benzoyloxyphenyliminyl.—Oxidation of α-benzyloxybenzylideneamino-oxyacetic acid (13), prepared from

the imidoyl chloride [7] (12) and sodium benzyl oxide, with persulphate gave a mixture of benzonitrile, benzaldehyde, benzamide, and benzyl benzoate. The same products, with the acetal (18), were obtained but in different proportions when the t-butyl perester (14) was heated in benzene (Table 2). Formation of (i) benzonitrile and benzaldehyde and (ii) benzamide and benzyl benzoate [*via* hydrolysis of the imine (16)] implies that fragmentation and intermolecular hydrogen abstraction are the main reactions of the iminyl (15), although it is difficult to distinguish between the latter process and dimerisation since benzyl benzoate and benzamide could be hydrolysis products of the corresponding azine. Only very weak e.s.r. spectra due to the iminyl could be detected when the perester (14) was heated in benzene solution, but addition of 2-methyl-2-nitrosopropane resulted in the detection of intense signals due to t-butyl benzoyl nitroxide [8] (17) (a_N 8.0 G). t-Butoxy t-butyl nitroxide [9] (a_N 27.1 G) was the only alkoxy nitroxide detected and hence the benzyloxyl radicals must be rapidly oxidised to benzaldehyde during the perester decomposition. The weaker signals, also present in the spectrum, we attribute to nitroxides formed by trapping of intermediate radicals derived from benzyloxyl and/or benzoyl. The most prominent of the weaker signals had hyperfine splittings (a_N 13.2, a_H 1.7 G) very similar to those of the α-benzoyloxybenzyl nitroxide [8,10] (19) independently generated from benzoyl peroxide and t-butyl phenyl nitrone (a_N 13.2, a_H 1.5 G).

Fragmentation of Iminyls.—Fragmentation of iminyls to nitriles [equation (i)] and alkyl or other radicals parallels that of alkoxyl radicals to ketones [equation (ii)]

$$R_2CN\cdot \longrightarrow RCN + R\cdot \quad \text{(i)}$$

$$R_3CO\cdot \longrightarrow R_2CO + R\cdot \quad \text{(ii)}$$

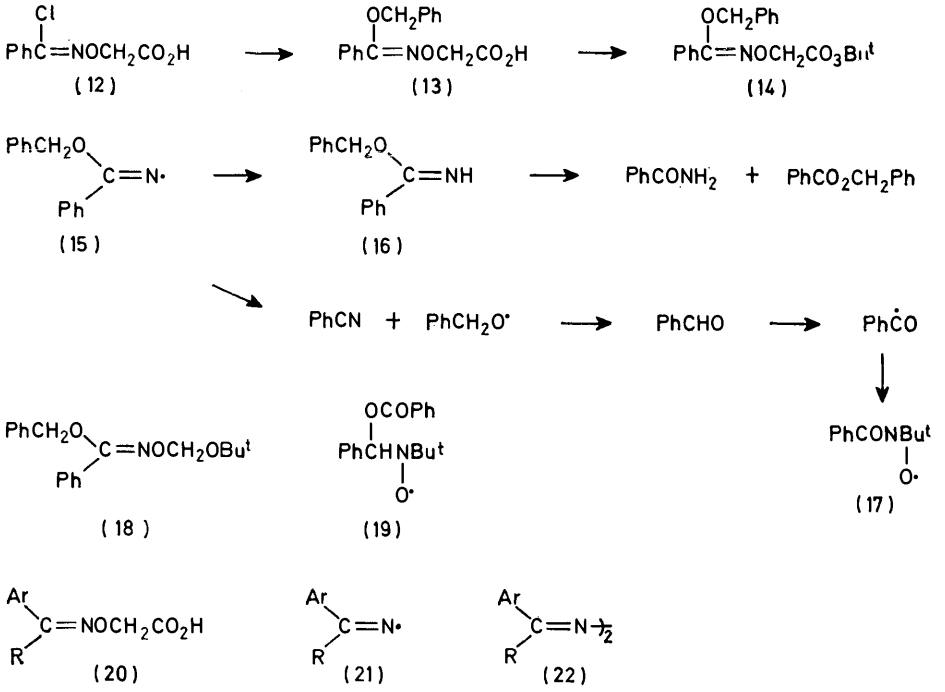
and alkyl radicals. It has been shown [11] by e.s.r.–kinetic measurements that loss of t-butyl from di-t-butyliminyl occurs at a rate similar to that at which t-butoxyl loses methyl. Ease of fragmentation depends largely on the nature [12] of the fragment radical, and to some extent is predictable from thermochemical data.[13] Thus, benzyl(phenyl)iminyl (21; R = $PhCH_2$, Ar = Ph) generated from the corresponding imino-oxyacetic acid (20; R = $PhCH_2$, Ar = Ph) with persulphate, gave benzonitrile (67%) and the dimer ($PhCH_2CH_2Ph$) of the fragment radical but the homologous iminyl (21; R = $PhCH_2CH_2$, Ar = Ph), similarly generated, gave no benzonitrile, only the corresponding azine (22; R = $PhCH_2$, Ar = Ph) and ketone. The heats of reaction of

TABLE 2

Products (%) from decomposition of t-butyl peresters (4) and (14)

Perester	Nitrile (3)	Acetal (7) or (18)	Triazole (10)	ArPh (6)	Other products
(4; $R^1 = R^2 = H$)	38	21	9.2	25	
(4; $R^1 = H$, $R^2 = Me$)	33	11	24	25	
(14)	19	28			(PhCHO) * 21 ($PhCONH_2$) 20 ($PhCO_2CH_2Ph$)

* Detected by t.l.c. but not isolated.



these fragmentations are estimated * to be endothermic by 12.6 and 25.8 kcal mol^{-1}, respectively. Fragmentation also prevailed over intramolecular hydrogen abstraction [15] with t-butyl-(*o*-tolyl)iminyl (21; R = Bu^t, Ar = *o*-MeC_6H_4) which gave *o*-toluonitrile in 53% yield but not with the methyl-*o*-tolyl homologue (21; R = Me, Ar = *o*-MeC_6H_4). Thermochemical data [13] indicate that fragmentation of the phenyldiazo(phenyl)iminyls (2) is an *exothermic* process (5.5 kcal mol^{-1}), hence the high yields of arenecarbonitrile produced from these radicals. The benzyloxy(phenyl)iminyl fragments to a small extent although its fragmentation is estimated to be more endothermic (by 4 kcal mol^{-1}) than that of phenylethyl(phenyl)iminyl (21; R = PhCH_2CH_2, Ar = Ph) which does not fragment to any detectable extent.

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 gel was used for chromatographic separations. Yields of arenecarbonitrile were estimated by measurement of the extinction coefficient of $\nu_{C\equiv N}$ in the i.r. spectra of the crude product mixtures in carbon tetrachloride solution.

Preparation of Ketones and Oximes.—β-Phenylpropiophenone was prepared from 2-phenylethylmagnesium bromide and benzonitrile (*cf.* ref. 16), and converted into its oxime by a standard procedure.

Phenylazobenzaldehyde oxime was prepared by nitrosation of benzaldehyde phenylhydrazone with isopentyl nitrite in ethanolic sodium ethoxide; [17] best yields of the substituted azo-oximes were obtained using isopentyl nitrite in pyridine.[18]

Preparation of Imino-oxyacetic Acids.—These were prepared from the appropriate oxime and chloroacetic acid as previously described.[2] The following are new. α-*Benzylbenzylideneamino-oxyacetic acid* (20; R = PhCH_2, Ar = Ph) formed needles, m.p. 107—109° (from chloroform–petrol) (Found: C, 71.3; H, 5.7; N, 5.4. $C_{16}H_{15}NO_3$ requires C, 71.35; H, 5.6; N, 5.2%), $\nu_{max.}$ 1 736 and 1 709 cm^{-1}, δ 4.20 (2 H, s, PhCH_2) and 4.78 (2 H, s, OCH_2). 1,3-*Diphenylpropylideneamino-oxyacetic acid* (20; R = PhCH_2CH_2, Ar = Ph) gave prisms, m.p. 75—77° (from chloroform–petrol) (Found: C, 72.0; H, 5.8; N, 5.2. $C_{17}H_{17}NO_3$ requires C, 72.05; H, 6.05; N, 4.95%), $\nu_{max.}$ 1 732 cm^{-1}, δ 3.02 (4 H, m, CH_2CH_2) and 4.76 (2 H, s, OCH_2). α-*Phenylazobenzylideneamino-oxyacetic acid* (1; R^1 = R^2 = H) yielded orange needles, m.p. 150—154° (from aqueous alcohol) (Found: C, 63.5; H, 4.5; N, 14.8. $C_{15}H_{13}N_3O_3$ requires C, 63.6; H, 4.65; N, 14.85%), $\nu_{max.}$ 1 720 cm^{-1}, δ 4.87 (2 H, s, OCH_2). p-*Methyl*-α-*phenylazobenzylideneamino-oxyacetic acid* (1; R^1 = Me, R^2 = H), afforded yellow needles, m.p. 145—147° (from aqueous alcohol) (Found: C, 64.7; H, 5.3; N, 14.0. $C_{16}H_{15}N_3O_3$ requires C, 64.65; H, 5.1; N, 14.15%), $\nu_{max.}$ 1 722 cm^{-1}, δ 2.40 (3 H, s, Me) and 4.91 (2 H, s, OCH_2). α-p-*Tolylazobenzylideneamino-oxyacetic acid* (1; R^1 = H, R^2 = Me) gave orange needles, m.p. 152—154° (from aqueous alcohol) (Found: C, 64.9; H, 5.4; N, 13.9. $C_{16}H_{15}N_3O_3$ requires C, 64.65; H, 5.1; N, 14.15%), $\nu_{max.}$ 1 720 cm^{-1}, δ 2.39 (3 H, s, Me) and 4.88 (2 H, s, OCH_2). p-*Methoxy*-α-*phenylazobenzylideneamino-oxyacetic acid* (1; R^1 = OMe, R^2 = H) formed orange needles, m.p. 126—128° (from aqueous alcohol) (Found: C, 61.6; H, 5.1; N, 13.6. $C_{16}H_{15}N_3O_4$ requires C, 61.35; H, 4.85; N, 13.4%), $\nu_{max.}$ 1 756 cm^{-1}, δ 3.82 (3 H, s, OMe) and 4.88 (2 H, s, OCH_2).

α-Aminobenzylideneamino-oxyacetic acid was prepared and converted into the acid (12) as described in ref. 7.

α-*Benzyloxybenzylideneamino-oxyacetic Acid* (13).—To a solution of sodium benzyl oxide in benzyl alcohol [from sodium (0.21 g) and benzyl alcohol (5 ml)], the acid (12) (0.5 g) in benzyl alcohol (2 ml) was added. The mixture was heated at 70° for 3 days and then aqueous sodium hydrogencarbonate solution was added. The excess of benzyl alcohol was removed by extraction with ether before the aqueous solution was acidified and then extracted with chloroform. The extracts were dried and evaporated to give the *acid* (13) (0.38 g, 57%) as needles, m.p. 110° (from chloroform–petrol) (Found: C, 67.1; H, 5.3; N, 4.7%; M^+, 285.100 1. $C_{16}H_{15}NO_4$ requires C, 67.4; H, 5.3; N, 4.9%; *M*, 285.100 1), $\nu_{max.}$ 1 722 and 1 705 cm^{-1}, δ (mixture of *syn*- and *anti*-isomers) 4.59 and 4.72 (total 2 H, each s, OCH_2Ph), 5.17 and 5.40 (total 2 H, each s, OCH_2CO_2H), and 7.28—7.90 (11 H, m, ArH and OH).

Preparation of t-Butyl Peresters of Imino-oxyacetic Acid.—These were prepared from the corresponding imino-oxyacetic acids, t-butyl hydroperoxide, and di-imidazolyl ketone.[2,19]

t-Butyl phenylazobenzylideneamino-oxyperacetate (4; R^1 = R^2 = H) was a red oil which slowly crystallised at −20° to give yellow needles, m.p. 43—47° (Found: C, 63.7; H, 6.0; N, 12.3. $C_{19}H_{21}N_3O_4$ requires C, 64.2; H, 5.95; N, 11.8%), $\nu_{max.}$ 1 785 cm^{-1}, δ 1.34 (9 H, s, Bu^t), 4.97 (2 H, s, OCH_2), 7.50br (8 H, s, ArH), and 7.89 (2 H, m, ArH). *t-Butyl* p-*tolylazobenzylideneamino-oxyperacetate* (4; R^1 = H, R^2 = Me) was an orange oil (Found: C, 64.8; H, 6.6; N, 11.6. $C_{20}H_{23}N_3O_4$ requires C, 65.05; H, 6.3; N, 11.35%), $\nu_{max.}$ 1 785 cm^{-1}, δ 1.34 (9 H, s, Bu^t), 2.41 (3 H, s, Me), 4.97 (2 H, s, OCH_2), 7.30 and 7.82 (4 H, each d, *J* 8.4 Hz, ArH of $C_6H_4CH_3$), and 7.50br (5 H, s, Ph). *t-Butyl* α-*benzyloxybenzylideneamino-oxyperacetate* (14) was an oil (Found: N, 4.1. $C_{20}H_{23}NO_5$ requires N, 3.9%), $\nu_{max.}$ 1 790 cm^{-1}, δ 1.32 (9 H, s, Bu^t), 4.6 (2 H, s, OCH_2Ph), 5.2 (2 H, s, OCH_2CO_3Bu^t), and 7.3—8.0 (10 H, m, ArH).

Oxidation of Imino-oxyacetic Acids with Persulphate.—These were carried out as previously described.[2,4]

α-Benzyl benzylideneamino-oxyacetic acid (1.08 g) gave (i) benzonitrile (275 mg, 67%) (estimated by i.r. measurement of C≡N of the crude reaction mixture); (ii) bibenzyl (160 mg, 44%), identical (i.r. ,m.p., R_F) with an authentic sample, and (iii) benzyl phenyl ketone (90 mg, 12%).

1,3-Diphenylpropylideneamino-oxyacetic acid (566 mg) gave (i) 1,3-diphenylpropan-1-one (122 mg, 30%), m.p. 65—66° (lit.,[20] 72—73°); (ii) 1,3-*diphenylpropan*-1-*one azine* (184 mg, 44.5%) as yellow spherules (from chloroform–petrol) or yellow needles (from acetic acid), m.p. 111—113° (Found: C, 86.4; H, 6.5; N, 6.8. $C_{30}H_{28}N_2$ requires C, 86.5; H, 6.8; N, 6.7%), δ 3.02 (8 H, m, CH_2CH_2), 7.20—7.49 (16 H, m, ArH), and 7.93 (4 H, m, *o*-ArH), identical (i.r., m.p., mass spectrum, and R_F) with an authentic sample prepared by heating an equimolar mixture of 1,3-diphenylpropan-1-one and its hydrazone in n-butanol overnight; and (iii) 2,4,6-triphenylpyrimidine (8 mg, 1.3%) identical with an authentic sample (see Part 3 [4]).

α-Phenylazobenzylideneamino-oxyacetic acid (920 mg)

* A value of 44.5 kcal mol^{-1} was used for $\Delta H°_f$ [$C_I(C_B)(C)_2(N_I)$]. This was derived from the known value [13] for $CH_3CH{=}N$. A similar value was used by Ingold *et al.*[11] while Crow *et al.*[14] used a larger one for their high temperature work.

gave (i) benzonitrile (110 mg, 53%); (ii) 2-benzoylamino-azobenzene (35 mg, 12%), orange needles, m.p. 120—123° (from methanol) (lit.,[21] 122°) (Found: C, 75.6; H, 5.0; N, 14.1%; M^+, 301.121 3. Calc. for $C_{19}H_{15}N_3O$: C, 75.75; H, 5.0; N, 13.95%; M, 301.121 5), $\nu_{max.}$ 3 340 and 1 654 cm^{-1}, δ 7.20—8.05 (13 H, m, ArH), 8.90 (1 H, dd, ArH), and 11.42br (1 H, s, NH), identical with an authentic sample prepared from nitrosobenzene and *N*-(*o*-aminophenyl)benzamide as described by Witt,[21] (iii) 1,3-diphenyl-1,2,4-triazole (10 mg, 2.3%) as rhombs, m.p. 75° (from methanol) (lit.,[3a] 79—81°) (Found: M^+, 221.095 5. Calc. for $C_{14}H_{11}N_3$: M, 221.095 3), *m/e* 221 (70%, M^+), 194 (7, $C_{13}H_{10}N_2$), and 91 (100, C_6H_5N), identical with an authentic sample;[3] and (iv) recovered acid (360 mg).

p-Methyl-α-phenylazobenzylideneamino-oxyacetic acid (240 mg) gave (i) *p*-toluonitrile (26 mg, 60%); (ii) 2-(*p*-toluoylamino)azobenzene (4 mg, 5.5%), as orange spherules, m.p. 117° (from petrol), $\nu_{max.}$ 3 350, 1 658, and 1 652 cm^{-1}, *m/e* 315 (3%, M^+), 210 (16), 119 (100), 105 (3), 91 (40), and 77 (16) identical with an authentic specimen; (iii) 1-*phenyl*-3-(p-*tolyl*)-1,2,4-*triazole* (12 mg, 13%), as needles, m.p. 64—66° (Found: M^+, 235.111 0. $C_{15}H_{13}N$ requires M, 235.110 9), $\nu_{max.}$ 3 195 (C–H of triazole ring) and 1 602 (C=N, C=C) cm^{-1}, δ 2.40 (3 H, s, Me), 7.23—7.79 (7 H, m, ArH), 8.09 (2 H, d, J 4.0 Hz, *o*-H of 3-*p*-tolyl), and 8.54 (1 H, s, 5-H), *m/e* 235 (70%, M^+), 208 (6, $C_{14}H_{12}N_2$), and 91 (100, C_6H_5N); and (iv) unchanged acid (130 mg).

α-*p*-Tolylazobenzylideneamino-oxyacetic acid (1.2 g) gave (i) benzonitrile (58%) and (ii) unchanged acid (500 mg); a product with R_F identical with that of the triazole obtained previously by oxidation of the imino-oxyacetic acid (1; R^1 = H, R^2 = Me) with persulphate was detected but not isolated.

p-Methoxy-α-phenylazobenzylideneamino-oxyacetic acid (63 mg) gave (i) *p*-methoxybenzonitrile (4.5 mg, 70%) and (ii) unchanged acid (48 mg).

α-Benzyloxybenzylideneamino-oxyacetic acid (250 mg) gave (i) benzonitrile (2.4 mg, 7%); (ii) benzamide (39 mg); and (iii) benzyl benzoate (11 mg), and a mixture of benzaldehyde and benzyl benzoate (14 mg). The yields, measured by n.m.r. using pivalonitrile as standard, were benzamide (17%), benzaldehyde (21%), and benzyl benzoate (17%).

Preparation of 2-(p-*Toluoylamino*)*azobenzene*.—*N*-(*o*-Nitrophenyl)-*p*-methylbenzamide[22] (16 g) was added to a mixture of iron powder (30 g) and 5% aqueous acetic acid (33 ml), and the mixture was heated on a water-bath for 1 h. The excess of acetic acid was neutralised by addition of sodium hydrogencarbonate solution. The precipitation was extracted with hot ethanol. Purification of the crude product *via* its hydrochloride gave N-(o-*aminophenyl*)-p-*methylbenzamide* (2.2 g), as plates, m.p. 153° (from methanol) (Found: C, 74.3; H, 6.2; N, 12.5. $C_{14}H_{14}N_2O$ requires C, 74.3; H, 6.25; N, 12.4%), $\nu_{max.}$ 3 435, 3 340, 3 290, and 1 640 cm^{-1}, δ 2.42 (3 H, s, Me), 3.75br (2 H, s, NH), 6.65—7.88 (8 H, m, ArH), and 8.0br (1 H, s, NH).

The above amine (2.26 g) was dissolved in acetic acid (20 ml) and ethanol (8 ml) and then nitrosobenzene (535 mg) was added. The solution, which changed from green to brown, was left for 16 h, before it was heated briefly and then cooled in ice. 2-(p-*Toluoylamino*)*azobenzene* separated as orange-brown needles (900 mg), m.p. 118—122° (from methanol) (Found: C, 76.0; H, 5.3; N, 13.4%; M^+, 315.137 4. $C_{20}H_{17}N_3O$ requires C, 76.15; H, 5.45; N, 13.3%; M, 315.137 1), $\nu_{max.}$ 3 350, 1 658, and 1 652 cm^{-1}, δ 2.43 (3 H, s, Me), 7.19—7.97 (12 H, m, ArH), 8.84 (1 H, dd, ArH), and 11.30br (1 H, s, NH), *m/e* 315 (28%, M^+), 210 (75), 119 (100), 105 (5), 91 (45), and 77 (22).

Decomposition of t-Butyl Peresters of Imino-oxyacetic Acids.—The peresters were decomposed in benzene solution under reflux and the products were isolated as previously described.[2]

t-Butyl phenylazobenzylideneamino-oxyperacetate (175 mg) gave (i) (*phenylazobenzylideneamino-oxy*)-*t-butoxymethane* (32 mg, 21%) as a red oil (Found: C, 69.2; H, 7.0; N, 13.5. $C_{18}H_{21}N_3O_2$ requires C, 69.45; H, 6.8; N, 13.5%), δ 1.25 (9 H, s, Bu^t), 5.48 (2 H, s, OCH_2), 7.38—7.60 (8 H, m, ArH), and 7.85br (2 H, m, *o*-ArH); (ii) 1,3-diphenyl-1,2,4-triazole (10 mg, 9.2%), identical with an authentic specimen; (iii) biphenyl (19 mg, 25%), as leaflets, m.p. 64—66° (after sublimation) (lit.,[3] 70.5°); and (iv) benzonitrile (19 mg, 37.6%).

t-Butyl *p*-tolylazobenzylideneamino-oxyperacetate (113 mg) gave (i) (p-*tolylazobenzylideneamino-oxy*)-*t-butoxymethane* (11 mg, 11%) as a red oil (Found: C, 70.2; H, 7.5; N, 12.5. $C_{19}H_{23}N_3O_2$ requires C, 70.15; H, 7.1; N, 12.9%), δ (two isomers) 1.23 and 1.25 (total 9 H, each s, Bu^t), 2.41 and 2.36 (total 3 H, each s, $ArCH_3$), 5.52 and 5.32 (total 2 H, each s, OCH_2), and 7.1—7.95 (9 H, m, ArH); (ii) benzonitrile (13 mg, 33%); (iii) 3-*phenyl*-1-(p-*tolyl*)-1,2,4-*triazole* (17 mg, 24%) as pale tan needles, m.p. 82—83.5° (from hexane) (Found: C, 76.8; H, 5.8; N, 17.8. $C_{15}H_{13}N_3$ requires C, 76.55; H, 5.55; N, 17.85%), δ 2.34 (3 H, s, Me), 7.13—7.62 (7 H, m, ArH), 8.18 (2 H, m, *o*-ArH), and 8.46 (1 H, s, 5-H), *m/e* 235 (100%, M^+), 208 (1), and 105.057 6 (63, $C_7H_7N^+$ requires *m/e* 105.057 8); and (iv) 4-methylbiphenyl (13 mg, 25%) as leaflets, m.p. 45° (from methanol) (lit.,[23] 47—48°).

t-Butyl α-benzyloxybenzylideneamino-oxyperacetate (300 mg) gave (i) (α-*benzyloxybenzylideneamino-oxy*)-*t-butoxymethane* (74 mg, 28%), b.p. 130° at 0.2 mmHg (air-bath temp.) (Found: C, 72.5; H, 7.1; N, 4.4%; M^+, 313.167 5. $C_{19}H_{23}NO_3$ requires C, 72.8; H, 7.4; N, 4.5%; M, 313.167 7), δ 1.21 (9 H, s, Bu^t), 5.21 (2 H, s, OCH_2Ph), 5.24 (2 H, s, OCH_2O), and 7.26—7.86 (10 H, m, 2Ph); (ii) benzyl benzoate (35.3 mg, 20%); (iii) benzamide (20.6 mg, 20%); (iv) benzaldehyde (trace); and (v) benzonitrile (16.3 mg, 19%), all identical (t.l.c. and n.m.r.) with authentic samples. The yields of products, except benzonitrile were estimated by n.m.r. measurement of the product mixture.

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