Iminyls. Part 3.[1] Formation of Triaryl-pyridines and -pyrimidines from Aryl-β-arylvinyliminyls

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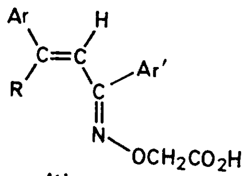
Aryl-β-arylvinyliminyls, produced by oxidation of the corresponding imino-oxyacetic acids with persulphate or by thermolysis of the t-butyl peresters of these acids, abstract hydrogen giving imines which dimerise and/or are hydrolysed to ketones. The bicyclic dimers so formed readily undergo oxidative fragmentation to triaryl-pyridines and/or -pyrimidines.

WITH a view to extending the scope of the synthetically useful cyclisation of phenyl(triarylvinyl)iminyls to triarylquinolines[1] a series of aryl-β-monoarylvinyl-iminyls has been generated, by (a) oxidation of the corresponding imino-oxyacetic acids (1) with persul-



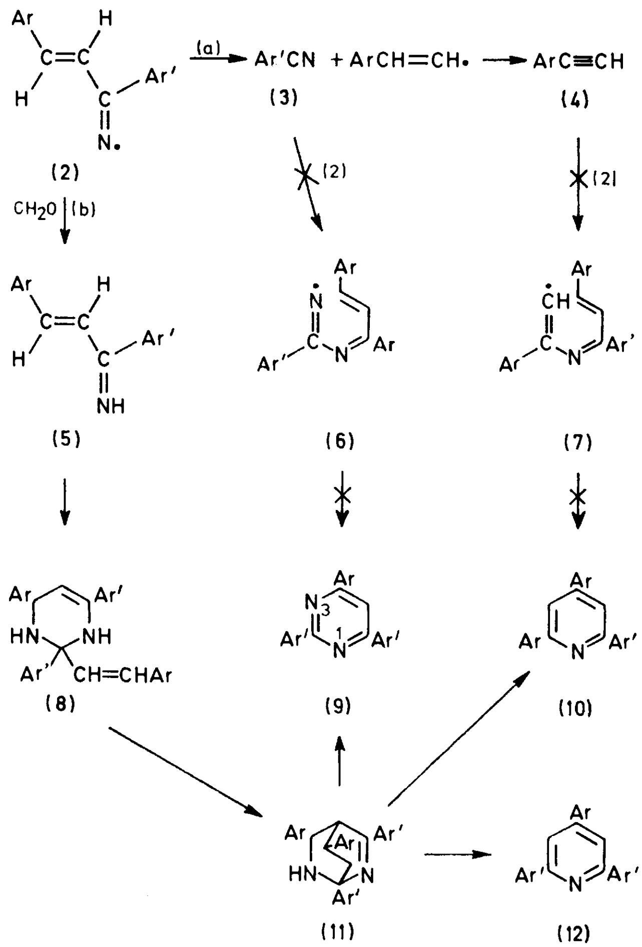
(1)

phate, and (b) thermolysis of the t-butyl peresters of these acids in benzene, and their behaviour examined.

Vinyliminyls (2) with only one β-aryl substituent do not cyclise to quinolines. Instead the parent ketone [and/or the acetal with method (b)] together with smaller amounts of triaryl-pyridines (10) and (12) and/or pyrimidines (9) are the main products (Table 1). Presumably, cyclisation of these radicals does not occur because of the *trans*-arrangement of the β-aryl and iminyl groups.

Although intramolecular addition of iminyl radicals to nitriles does occur in certain cases[2] we discount, for the following reasons, the possibility that the triaryl-pyridines (10) and (12) and -pyrimidines (9) arise by fragmentation of the iminyl (2) to arenecarbonitrile (3) and (after oxidation) arylacetylene (4) followed by addition of iminyl (2) to these products as outlined in the sequence of reactions [(3) ⟶ (6) ⟶ (9)] and [(4) ⟶ (7) ⟶ (10)] in Scheme 1, path (a). (i) Thermolysis of the t-butyl perester of diphenylmethyleneamino-oxy-acetic acid in benzonitrile and in acetonitrile gave essentially the same product distribution as that obtained using benzene as solvent; no products arising from addition of diphenyliminyl to the nitriles were detected. (ii) When the β-phenylvinyliminyl (2; Ar = Ph, Ar′ = *p*-$MeOC_6H_4$) was generated from the corresponding t-butyl perester by thermolysis in benzene and in benzo-nitrile the product yields were almost identical. (iii) The isomeric β-arylvinyliminyls (2; Ar = Ph, Ar′ = *p*-MeC_6H_4 and Ar = *p*-MeC_6H_4, Ar′ = Ph) gave (as determined by n.m.r. and mass spectra) 1 : 1 mixtures of triarylpyridines (10) and (12) (Table 1); this result cannot be accounted for by Scheme 1, route (a).

We consider that the parent ketone and the heterocycles (9), (10), and (12) are all derived from the imine (5), formed from the iminyl (2) by hydrogen abstraction (from formaldehyde) [path (b)]. The imine (5; Ar = Ar′ = Ph) has been generated previously by Piper and Wright[3] from cinnamonitrile and phenylmagnesium



SCHEME 1

bromide, and was found to dimerise readily to the diazabicyclo[2.2.2]octene (11; Ar = Ar′ = Ph), oxidation of which with sulphur at 190° gave mixtures of triphenyl-pyridine and -pyrimidine. We have prepared the bicyclic amine (11) by the published route, confirmed its structure (previously based on degradation studies) by spectroscopic analyses (see Experimental section), and shown that it is not present in the product mixture obtained on persulphate oxidation of the imino-oxy-acetic acid precursor of the iminyl (2; Ar = Ar′ = Ph) nor in that from the thermal decomposition of the corresponding t-butyl perester in benzene. However, this is not an unexpected result since the bicyclic amine (11; Ar = Ar′ = Ph) was readily oxidised by persulphate in aqueous acetonitrile solution to a mixture of the pyridine (12; Ar = Ar′ = Ph) (50%) and pyrimidine (9; Ar = Ar′ = Ph) (9%), and by di-t-butyl peroxide cleanly to 2,4,6-triphenylpyrimidine (88%). The relative yields of triaryl-pyridine and -pyrimidine on oxidation of the bicyclic amine (11) clearly depend on the oxidising agent and the reaction conditions (temperature, solvent, *etc.*) but we have not pursued this aspect. The elucidation of the substitution patterns of aryl groups about the pyrimidine and pyridine nuclei in the triarylpyrimidines (9) and triarylpyridines (10) and (12) listed in Table 1 was achieved by analysis of the aromatic regions of their n.m.r. spectra (Tables 2 and 3). Thus, the *ortho*-protons of aryl substituents at position 2 in the pyrimidines resonate characteristically between δ 8.75 and 8.55 whereas the corresponding protons of the 4-Ar and 6-Ar rings in the pyrimidines and the 2-Ar and 6-Ar rings in the pyridines appear between δ 8.10 and 8.26. *meta*- and *para*-protons of all three rings resonate between δ 7.00 and 7.80. Therefore, the chemical shift and multiplicity of the *ortho*-proton signals define the substitution pattern about the heterocyclic rings.

Methyl-β-phenylvinyliminyl (13; R = H, R′ = Me), generated from the corresponding imino-oxyacetic acid in the usual way,[4] gave a complex mixture of products from which only the corresponding azine (13%) and parent ketone (7%) (formed by hydrolysis of the imine) were isolated and identified. Similarly no triarylpyridines nor -pyrimidines were obtained from the β-methyl-β-phenylvinyliminyl (13; R = Me, R′ = Ph), 2,4-diphenylpyridine (15), and dypnone (β-methylchalcone) being the main products, albeit in low yield. The diphenylpyridine is probably formed by reaction of the imine (14) with formaldehyde (from β-scission of the

TABLE 1

Products (%) obtained from vinyliminyls

Iminyl (2) or (13)	Method of production	Acetal	Pyridines (10) + (12)	Pyrimidine (9)	Ketone
(2; Ar = Ar′ = Ph)	*a*		4	11	21
(2; Ar = *p*-MeOC$_6$H$_4$, Ar′ = Ph)	*a*			4.6	52
(2; Ar = Ph, Ar′ = *p*-MeOC$_6$H$_4$)	*a*			6.4	38
(2; Ar = *p*-MeC$_6$H$_4$, Ar′ = Ph)	*a*		1.1 †	7.4	20
(2; Ar = Ph, Ar′ = *p*-MeC$_6$H$_4$)	*a*		1.1 †	6.0	31
(2; Ar = Ar′ = Ph)	*b*	18		§	7.0
(2; Ar = Ph, Ar′ = *p*-MeOC$_6$H$_4$)	*b*	23		5.0	10
	b *	29.5		4.2	§
(13; R = Me, R′ = Ph)	*a*		11.3 ‡		15
(13; R = H, R′ = Me)	*a*				7 ¶

* Thermolysis in benzonitrile. † 1 : 1 Mixture of isomers. ‡ Refers to yield of (15). § Detected by t.l.c. but not isolated. ¶ Accompanied by 13% of the corresponding azine. [a] Persulphate oxidation of amino-oxyacetic acid. [b] Thermal decomposition of t-butyl perester of imino-oxyacetic acid.

TABLE 2

N.m.r. data for pyrimidines (9)

Compound	2-Ar *o*-H	2-Ar *m*-H	2-Ar *p*-H	4-Ar *o*-H	4-Ar *m*-H	4-Ar *p*-H	5-H	6-Ar *o*-H	6-Ar *m*-H	6-Ar *p*-H	Other signals
(9; Ar = Ar′ = Ph)	8.72 (m)	7.50 (m)	7.50 (m)	8.26 (m)	7.50 (m)	7.50 (m)	7.94 (s)	8.26 (m)	7.50 (m)	7.50 (m)	
(9; Ar = *p*-MeOC$_6$H$_4$, Ar′ = Ph)	8.75 (m)	7.54 (m)	7.54 (m)	8.25 (d*)	7.05 (d*)		7.93 (s)	8.25 (m)	7.54 (m)	7.54 (m)	3.86 (3 H, s, OMe)
(9; Ar = Ph, Ar′ = *p*-MeOC$_6$H$_4$)	8.62 (d*)	7.00 (d*)		8.21 (m)	4.79 (m)	7.49 (m)	7.81 (s)	8.21 (d*)	7.00 (d*)		3.85 (6 H, s, 2OMe)
(9; Ar = *p*-MeC$_6$H$_4$, Ar′ = Ph)	8.73 (m)	7.53 (m)	7.53 (m)	8.19 (d*)	7.33 (d*)		7.96 (s)	8.25 (m)	7.53 (m)	7.53 (m)	2.44 (3 H, s, Me)
(9; Ar = Ph, Ar′ = *p*-MeC$_6$H$_4$)	8.55 (d*)	7.26 (d*)		8.17 (m)	7.46 (m)	7.49 (m)	7.86 (s)	8.12 (d*)	7.26 (d*)		2.43 (6 H, s, 2Me)

* *J* 8.5 Hz.

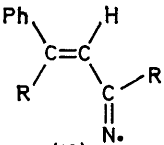
TABLE 3

N.m.r. data for pyridines (10), (12), and (15)

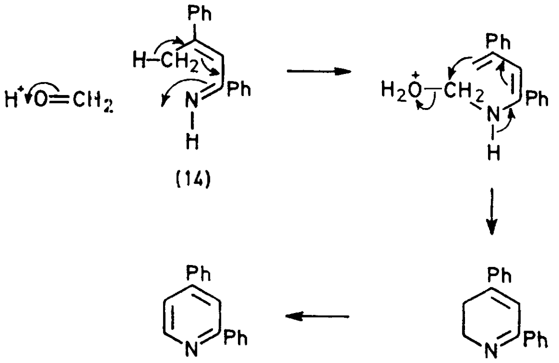
Compound	2- and 6-Ar *o*-H	*m*- and *p*-H	3- and 5-H	4-Ar	Other signals
(10; Ar = Ar′ = Ph)	8.18 (dd) *	7.4 —7.7 (m)	7.86	7.4 —7.7 (m)	
(10; Ar = *p*-MeC$_6$H$_4$, Ar′ = Ph) [a]	8.13 (m)	7.24—7.68 (m)	7.84 [b]	7.24—7.68 (m)	2.42 (Me)
(12; Ar = *p*-MeC$_6$H$_4$, Ar′ = Ph) [a]	8.13 (m)	7.24—7.68 (m)	7.86 [b]	7.24—7.68 (m)	2.42 (Me)
(10; Ar = Ph, Ar′ = *p*-MeC$_6$H$_4$) [a]	8.10 (d) †	7.24—7.80 (m)	7.24—7.80	7.24—7.80 (m)	2.22(Me)
(12; Ar = Ph, Ar′ = *p*-MeC$_6$H$_4$) [a]	8.10 (d) †	7.24—7.80 (m)	7.24—7.80	7.24—7.80 (m)	2.22 (Me)
(15)	8.04 (m)	7.46—7.70 (m)	8.08 (5-H) 7.92 (3-H)	7.46—7.70 (m)	8.73 (1 H, d, *J* 2.5 Hz, 6-H)

* *J* 2 and 7 Hz. † *J* 8.0 Hz. [a] 1 : 1 Mixture measured. [b] These values can be exchanged.

initial imino-oxymethyl radical) as indicated in Scheme 2.


(13)

The difference in the nature of the products derived from the two last mentioned iminyls and those obtained


(14)
(15)

SCHEME 2

from the other β-phenylvinyliminyls is due to a difference in reactivity of the corresponding imines and not of the iminyls. Dimerisation of the least hindered styryliminyl (**13**; R = H, R' = Me) does occur to some extent but the main reaction in all cases is hydrogen abstraction to give the imine. The most likely source of abstractable hydrogen is formaldehyde produced during the fragmentation stage

E.s.r. spectra (a_N 10.0 G, a_H unresolved, *g* 2.003 5) of the iminyls (2; Ar = Ar' = Ph and Ar = *p*-MeOC$_6$H$_4$, Ar' = Ph) were easily detected when their t-butyl perester precursors were heated at 75° in benzene in the spectrometer.

EXPERIMENTAL

I.r. spectra were measured as KBr discs and n.m.r. spectra using deuteriochloroform as solvent, unless stated otherwise. Chromatographic separations were achieved using Merck GF$_{254}$ silica gel. Petrol refers to light petroleum, b.p. 60—80°.

Preparation of Ketones and Oximes.—Chalcone,[5] benzylideneacetone,[6] 4-methylchalcone,[7] 4-methoxychalcone,[7] 4'-methylchalcone,[7] 4'-methoxychalcone,[7] and dypnone [8] were prepared by literature methods.

Substituted chalcone oximes and dypnone oxime were prepared [9] by heating the ketone under reflux for 15 h with hydroxylamine hydrochloride in methanol containing a few drops of hydrochloric acid.

Preparation of Imino-oxyacetic Acids.—These were prepared from the oxime, chloroacetic acid, and sodium hydroxide in aqueous ethanol.[4] The following are new. α-(β-*Methyl*-β-*phenylvinyl*)*benzylideneamino-oxyacetic acid* (1; Ar = Ar' = Ph, R = Me) formed needles, m.p. 123—124° (from chloroform–petrol) (Found: C, 73.0; H, 5.7; N, 4.5. $C_{18}H_{17}NO_3$ requires C, 73.2; H, 5.8; N, 4.75%), $\nu_{max.}$ 1 729 and 1 710 cm^{-1}, δ 1.88 (3 H, d, *J* 1.2 Hz, Me), 4.70 (2 H, s, OCH$_2$), and 6.58 (1 H, m, –CH=); 1-(*benzylidenemethyl*)*ethylideneamino-oxyacetic acid* gave needles, m.p. 127—129° (from chloroform–petrol) (Found: C, 66.0; H, 6.2; H, 6.5. $C_{12}H_{13}NO_3$ requires C, 65.75; H, 6.0; N, 6.4%), $\nu_{max.}$ 1 720 cm^{-1}, δ 2.12 (3 H, s, Me) and 4.67 (2 H, s, OCH$_2$); α-(β-*phenylvinyl*)*benzylideneamino-oxyacetic acid* (1; Ar = Ar' = Ph, R = H) afforded leaflets, m.p. 117—120° (from chloroform–petrol) (Found: C, 72.8; H, 5.3; N, 5.0. $C_{17}H_{15}NO_3$ requires C, 72.6; H, 5.35; N, 5.0%), $\nu_{max.}$ 1 721 and 1 702 cm^{-1}, δ 4.77 (2 H, s, OCH$_2$); α-(β-4-*methylphenylvinyl*)*benzylideneamino-oxyacetic acid* (1; Ar = *p*-MeC$_6$H$_4$, Ar' = Ph, R = H), gave needles, m.p. 128—131° (from chloroform–petrol) (Found: C, 72.9; H, 6.0; N, 5.0. $C_{18}H_{17}NO_3$ requires C, 73.2; H, 5.8; N, 4.75%), $\nu_{max.}$ 1 721 and 1 700 cm^{-1}, δ 2.35 (3 H, s, Me) and 4.83 (2 H, s, OCH$_2$); 4-*methyl*-α-(β-*phenylvinyl*)-*benzylideneamino-oxyacetic acid* (1; Ar = Ph, Ar' = *p*-MeC$_6$H$_4$, R = H) had m.p. 119—122° (from chloroform–petrol) (Found: C, 72.9; H, 6.0; N, 5.0. $C_{18}H_{17}NO_3$ requires C, 73.2; H, 5.8; N, 4.75%), $\nu_{max.}$ 1 718 and 1 710 cm^{-1}, δ 2.41 (3 H, s, Me) and 4.83 (2 H, s, OCH$_2$); α-(β-4-*methoxyphenylvinyl*)*benzylideneamino-oxyacetic acid* (1; Ar = *p*-MeOC$_6$H$_4$, Ar' = Ph, R = H), formed pale yellow needles, m.p. 138—141° (from chloroform–petrol) (Found: C, 69.4; H, 5.7; N, 4.7. $C_{18}H_{17}NO_4$ requires C, 69.45; H, 5.5; N, 4.5%), $\nu_{max.}$ 1 727 cm^{-1}, δ 3.80 (3 H, s, OMe) and 4.81 (2 H, s, OCH$_2$); 4-*methoxy*-α-(β-*phenylvinyl*)*benzylideneamino-oxyacetic acid* (1; Ar = Ph, Ar' = *p*-MeOC$_6$H$_4$, R = H), yielded needles, m.p. 120—121° (from benzene–petrol) (Found: C, 69.7; H, 5.7; N, 4.8. $C_{18}H_{17}NO_4$ requires C, 69.45; H, 5.5; N, 4.5%), $\nu_{max.}$ 1 706 cm^{-1}, δ 3.82 (3 H, s, OMe) and 4.80 (2 H, s, OCH$_2$).

Preparation of t-Butyl Peresters of Imino-oxyacetic Acids. (cf. *ref.* 10).—*t-Butyl* α-(β-*phenylvinyl*)*benzylideneamino-oxyperacetate.* To a stirred ice-cold solution of the appropriate imino-oxyacetic acid (5.62 g, 0.02 mol) in tetrahydrofuran (40 ml) under nitrogen di-imidazolyl ketone (6 g, 0.037 mol) was added in one portion. Stirring was continued for 1 h before t-butyl hydroperoxide (2.25 g, 0.025 mol) was added dropwise to the mixture maintained at 0°. After a further 1 h at 0° the solution was diluted with ether, and the ethereal solution was washed successively with water, 2M-hydrochloric acid, sodium hydrogen-carbonate solution, and water. Evaporation of the dried solution gave the *t-butyl peracetate* (5.75 g, 82%). An analytical sample was prepared by column chromatography on silica at 0—5° using petrol--chloroform (2 : 3) as irrigant (Found: C, 71.1; H, 6.7; H, 4.3. $C_{21}H_{23}NO_4$ requires C, 71.35; H, 6.55; N, 3.95%), $\nu_{max.}$ 1 794 cm^{-1}, δ 1.32 (9 H, s, Bu^t) and 4.86 (9 H, s, OCH$_2$).

Similarly prepared was *t-butyl* α-(β-4-*methoxyphenylvinyl*)*benzylideneamino-oxyperacetate* as a pale yellow oil (Found: C, 68.7; H, 6.6; N, 3.5. $C_{22}H_{25}NO_5$ requires C, 68.9; H, 6.55; N, 3.65%), $\nu_{max.}$ 1 790 cm^{-1}, δ 1.33 (9H, s, Bu^t), 3.82 (3 H, s, OMe), and 4.85 (2 H, s, OCH$_2$).

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

1-(Benzylidenemethyl)ethylideneamino-oxyacetic acid (876 mg) gave (a) benzylideneacetone (40 mg, 7%), and (b) benzylideneacetone azine (73 mg, 13%), yellow needles, m.p. 168° (lit.,[11] 160°) (from methyl ethyl ketone) (Found: M^+, 288.162 9. Calc. for $C_{20}H_{20}N_2$: *M*, 288.162 6), δ 2.18 (6 H, s, 2Me), 7.08 (4 H, s, CH=CH), and 7.25—7.65 (10 H, m, ArH).

α-(β-Phenylvinyl)benzylideneamino-oxyacetic acid (1 g) gave (a) chalcone (160 mg, 21%), (b) 2,4,6-triphenylpyrimidine (60 mg, 11%), needles m.p. 190—190.5° (lit.,[12] 185—186°) (from methanol) (Found: C, 85.8; H, 5.2; N, 9.1. Calc. for $C_{22}H_{16}N_2$: C, 85.7; H, 5.25; N, 9.1%), and (c) 2,4,6-triphenylpyridine (20 mg, 4%), needles, m.p. 137—140° (lit.,[13] 138°) (from methanol) (Found: C, 89.7; H, 5.6; N, 4.7. Calc. for $C_{23}H_{17}N$: C, 89.85; H, 5.55; N, 4.55%).

α-(β-4-Methoxyphenylvinyl)benzylideneamino-oxyacetic acid (9.33 g) gave (a) 4-methoxychalcone (3.13 g, 52%), (b) *4-p-methoxyphenyl-2,6-diphenylpyrimidine* (210 mg, 4.6%), needles, m.p. 132—136° (from acetic acid) (Found: C, 81.6; H, 5.6; N, 8.0. $C_{23}H_{18}N_2O$ requires C, 81.65; H, 5.35; N, 8.3%), and (c) unchanged acid (900 mg).

4-Methoxy-α-(β-phenylvinyl)benzylideneamino-oxyacetic acid (6.22 g) gave (a) 4′-methoxychalcone (1.62 g, 38%); (b) *2,6-bis-p-methoxyphenyl-4-phenylpyrimidine* (211 mg, 6.4%), needles, m.p. 135—138° (from acetic acid) (Found: C, 78.1; H, 5.6; N, 7.6. $C_{24}H_{20}N_2O_2$ requires C, 78.25; H, 5.45; N, 7.6%), and (c) unchanged acid (600 mg).

α-(β-4-Methylphenylvinyl)benzylideneamino-oxyacetic acid (11.8 g) gave (a) 4-methylchalcone (1.63 g, 20%); (b) *2,6-diphenyl-4-p-tolylpyrimidine* (423 mg, 7.4%), needles, m.p. 148—150° (from acetic acid) (Found: C, 85.4; H, 5.5; N, 8.6. $C_{23}H_{18}N_2$ requires C, 85.7; H, 5.65; N, 8.7%); (c) an equimolar mixture (6.3 mg, 1.1%) of 2-phenyl-4,6-di-*p*-tolylpyridine (Found: M^+, 335.166 8. Calc. for $C_{25}H_{21}N$: *M*, 335.167 3) and 2,6-diphenyl-4-*p*-tolylpyridine (Found: M^+, 321.151 5. Calc. for $C_{24}H_{19}N$: *M*, 321.151 7), plates, m.p. 113—115° (from methanol) (lit.,[14,15] 138 and 159—160°, respectively), and (d) unchanged acid (1.2 g).

4-Methyl-α-(β-phenylvinyl)benzylideneamino-oxyacetic acid (11.8 g) gave (a) 4′-methylchalcone (2.44 g, 31%), (b) *4-phenyl-2,6-di-p-tolylpyrimidine* (349 mg, 6%), needles, m.p. 176—177° (from acetic acid) (Found: C, 86.0; H, 6.3; N, 8.2. $C_{24}H_{20}N_2$ requires C, 85.7; H, 6.0; N, 8.35%); (c) an equimolar mixture (7.0 mg, 1.1%) of 2,4-diphenyl-6-*p*-tolylpyridine (Found: M^+, 321.151 5. Calc. for $C_{24}H_{19}N$: *M*, 321.151 7) and 4-phenyl-2,6-di-*p*-tolylpyridine (Found: M^+, 335.167 1. Calc. for $C_{25}H_{21}N$: *M*, 335.167 3) as prisms, m.p. 126—131° (from methanol) (lit.,[16] 121 and 158—159°, respectively, and (d) unchanged acid (1.2 g).

α-(β-Methyl-β-phenylvinyl)benzylideneamino-oxyacetic acid (1.2 g) gave (a) dypnone (130 mg, 15%) and (b) 2,4-diphenylpyridine (104 mg, 11.3%), an oil (Found: M^+, 231. Calc. for $C_{17}H_{13}N$: *M*, 231), $\nu_{max.}$ 1 605, 1 595, and 1 580 cm^{-1}. Its picrate formed yellow leaflets, m.p. 185° (from alcohol) (lit.,[17] 187°) (Found: C, 60.2; H, 3.8; N, 12.3. Calc. for $C_{23}H_{16}N_4O_7$: C, 60.0; H, 3.5; N, 12.15%).

Other Oxidations.—(i) 1,3,5,8-Tetraphenyl-2,6-diazabicyclo[2.2.2]octene (83 mg) was dissolved in acetonitrile (10 ml) and water (2 ml) by heating under reflux. Potassium persulphate (60 mg) was added in one portion and the mixture was boiled for 0.5 h, cooled, and filtered. The filtrate was concentrated under reduced pressure to remove acetonitrile, and the resulting aqueous solution was extracted with ether. Evaporation of the dried ($MgSO_4$) ethereal extracts gave a residue which, after chromatography on silica and crystallisation, yielded 2,4,6-triphenylpyridine (28 mg, 50%) and -pyrimidine (5 mg, 9%).

(ii) 1,3,5,8-Tetraphenyl-2,6-diazabicyclo[2.2.2]oct-2-ene (100 mg) in di-t-butyl peroxide was heated under reflux for 2.5 h. Removal of solvent followed by chromatographic purification of the residue gave 2,4,6-triphenylpyrimidine (65 mg, 88%).

Decomposition of t-Butyl Peresters.—t-Butyl α-(β-phenylvinyl)benzylideneamino-oxyperacetate (1.36 g) in benzene (40 ml) was heated under nitrogen for 2 h. Evaporation of solvent followed by chromatography of the residue with petrol–chloroform gave (a) *α-(β-phenylvinyl)benzylideneamino-oxy-t-butoxymethane* (200 mg, 18%), an oil (Found: C, 78.3; H, 7.9; N, 4.4. $C_{20}H_{23}NO_2$ requires C, 77.65; H, 7.5; N, 4.55%), δ (two isomers 14 : 86) 1.18 and 1.32 (total 18 H, each s, Bu^t), 5.26 and 5.45 (total 4 H, each s, OCH_2), 6.76 (total 2 H, d, *J* 17 Hz, CH=), 7.1 (total 20 H, m, ArH), and 7.62 (total 2 H, d, *J* 17 Hz, CH=), (b) chalcone (54 mg, 7%), and (c) 2,4,6-triphenylpyrimidine (t.l.c. detection). When the perester was heated in cumene at 80, and at 150°, there was no significant change in the product distribution.

t-Butyl α-(β-4-methoxyphenylvinyl)benzylideneamino-oxyperacetate (50 mg) gave (a) *α-(β-4-methoxyphenylvinyl)-benzylideneamino-oxy-t-butoxymethane* (10 mg, 23%), an oil (Found: C, 74.7; H, 7.7; N, 3.9. $C_{12}H_{25}NO_3$ requires requires C, 74.3; H, 7.4; N, 4.15%), δ 1.32 (9 H, s, Bu^t), 3.78 (3 H, s, OMe), 5.44 (2 H, s, OCH_2), 6.68 (1 H, d, *J* 17 Hz, CH=), 7.49 (1 H, d, *J* 17 Hz, CH=), and 6.82—7.60 (9 H, m, ArH), (b) 4-methoxychalcone (3 mg, 10%), and (c) 2,6-diphenyl-4-*p*-methoxyphenylpyrimidine (1 mg, 5%), m.p. 134—136°.

Thermolysis of this perester (383 mg) in benzonitrile (20 ml) at 85° for 1.5 h gave (a) the acetal (100 mg, 29.5%), (b) the pyrimidine (7 mg, 4%), and (c) 4-methoxychalcone.

t-Butyl diphenylmethyleneamino-oxyperacetate (981 mg) heated in benzonitrile (60 ml) at 85° for 1.5 h gave, after chromatography of the product mixture, (a) benzophenone azine (*ca.* 20%), (b) benzophenone (*ca.* 40%), (c) diphenylmethyleneamino-oxy-t-butoxymethane (*ca.* 25%); (d) benzophenone *N*-diphenylmethylimine (18 mg, 3%), m.p. 152—153° (lit.,[18] 153°) (from methanol) (Found: M^+, 347. Calc. for $C_{26}H_{21}N$: *M*, 247); and (e) an unidentified product (30 mg) showing M^+ 296 ($C_{21}H_{16}N_2$).

The perester (981 mg) heated in acetonitrile at 85° for 1.5 h gave, after chromatography, benzophenone, benzophenone azine, diphenylmethyleneamino-oxy-t-butoxymethane (not collected), and *benzophenone N-cyanomethylimine* (80 mg, 13%) as an oil (Found: M^+, 220. $C_{15}H_{12}N_2$ requires *M*, 220), $\nu_{max.}$ 2 260, 1 655, and 1 620 cm^{-1}, δ 4.20 (2 H, s, CH_2) and 7.0—7.8 (10 H, m, ArH).

1,3,5,8-Tetraphenyl-2,6-diazabicyclo[2.2.2]oct-2-ene.—This was prepared from phenylmagnesium bromide and cinnamonitrile. It formed prisms, m.p. 180° (lit.,[3] 180—182°) (from acetonitrile), $\nu_{max.}$ 3 300 cm^{-1}, δ_H 1.90 (1 H, s, NH, exchanges with D_2O), 1.83 (1 H, dd, *J* 13.5 and 5.5 Hz, 7-H), 2.70 (1 H, dd, *J* 13.5 and 10 Hz, 7-H), 3.27 (1 H, dd, *J* 5.5, and 1.5 Hz, 8-H), 3.60 (1 H, dd, *J* 2 and 1.5 Hz, 4-H), 4.10 (1 H, d, *J* 2 Hz, 5-H), 6.77—7.80 (18 H, m, ArH), and 8.21 (2 H, dd, *o*-H of 3-Ph), coupling constant assignments made after spin-decoupling measurements, δ_C 35.0 (C-4), 42.90 (C-7), 47.38 (C-8), 57.75 (C-5), 75.03 (C-1), 126.58, 127.05, 127.36, 128.26, 129.29, 129.63, and 130.11 (all CH of Ph), 137.53 (quaternary C of 3-Ph), 142.40, 144.06, 145.43 (all quaternary C of 1-, 5-, and 8-Ph), 173.65 (C-3), assignments based on ' off-resonance ' and ' noise decoupled ' spectra.

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