Intramolecular Cyclisation of Iminoxyl Radicals

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Iminyl radicals, generated by oxidation of the corresponding *O*-carboxymethoximes with persulphate, do not cyclise onto an adjacent azo group but the structurally related iminoxyls cyclise to give indazoles. ESR evidence is presented for the intramolecular addition of iminoxyl radicals to carbon–carbon double bonds and to aryl rings.

Iminyls cyclise onto an adjacent aromatic ring¹ or carbon–carbon double bond² given favourable geometry. In principle, cyclisation onto other unsaturated groups is also possible. Accordingly, we have extended our previous investigations² to iminyls of type 4.

The iminyl precursors³ most suitable for chemical studies are methylene-imino-oxyacetic acids 3 and their derivatives. These are usually prepared from the corresponding ketones 1 *via* the oximes 2 thus providing the initial synthetic objectives of the work.

Precursors of *o*-azo-, *o*-azoxy- and *o*-imino-diphenyliminyls. Although the ketones 1a, 1b, 1e⁴ were readily prepared, numerous attempted condensa-

tions with hydroxylamine, methoxyamine, and amino-oxyacetic acid, under forcing conditions, failed to yield the desired products. The oximes 2a and 2b were eventually prepared⁵ from the *o*-aminoketoximes 5a and 5b by condensation with nitrosobenzene and converted into 3a and 3b in the usual way.³ However, oxidation with aqueous persulphate gave no major product, and the many minor coloured products were not investigated. Condensation of the amino-ketoximes 5a and 5b with benzaldehyde failed to give the desired *o*-imino-ketoximes 2c and 2d. Instead, the dihydroquinazoline *N*-oxides 6a and 6b were formed as earlier reported. Confirmation of structure 6b was achieved by ¹³C NMR spectroscopy. In particular the signal at δ 79.55 (doublet) is attributed to C–2. The imino carbon of 2c would be expected to resonate at lower field. Oxidation of the dihydroquinazoline *N*-oxides 6a and 6b to 8a and 8b apparently proceeds *via* the corresponding nitroxides 7a and 7b. Thus, treatment of 6a and 6b with lead tetra-acetate in the cavity of an ESR

Scheme 1. 1a–4a, X=Y=N=N, R¹=R²=Ph; 1b–4b, X=Y=N=N, R¹=Ph, R²=Me; 1c–4c, X=Y=N=CH, R¹=R²=Ph; 1d–4d, X=Y=N=CH, R¹=Ph, R²=Me; 1e, X=Y=N=N⁺(O[–]), R¹=Me, R²=Ph.

Scheme 2. 5a–8a, R=Ph; 5b–8b, R=Me.

Scheme 3. 9a–14a, R = Ph; 9b–14b, R = Me.

spectrometer led to the detection of the nitroxides 7b, $a_{N-3}=9.25$ and $a_{N-1}=2.5$ G, and 7a, $a_{N-3}=7.25$, $a_{N-1}=3.55$, $a_H=1.0$ G. The broad lines of the former spectrum (~ 1.25 G) prevented resolution of the proton splitting. The differences in the a_{N-1} values of the two spectra is surprising and at present unexplained.

Following these failures to observe intramolecular addition of iminyls to azo and imino groups attention was turned to the possibility of adding the cor-

responding iminoxyl radicals to adjacent multiple bonds. Oximes are potential precursors of both iminyls and iminoxyls and several suitable examples with adjacent, azo, alkenyl and aryl groups were available from this and earlier work.^{1,2}

o-(Phenylazo)phenylmethylenimineoxyls. Treatment of *o*-phenylazobenzophenone oxime 9a with lead tetra-acetate at -60°C in the cavity of an ESR spectrometer gave a weak spectrum of the corresponding iminoxyl 10a, $a_N=31$ G. The spectrum

Table 1. ESR data on radicals derived from oximes 15.

Oxime	Method ^a	Temp. °C	a_N (G)	Radical type
15a	a	20	12.5	Dialkyl nitroxide 20
	a	-60	19.75 5.4(1H) (Ha); 1.2(1H) (Hb)	Bicyclic nitroxide 18a
	b	-40	19.75 5.25(1H) (Ha); 1.25(1H) (Hb)	Bicyclic nitroxide 18a
15b	a	-60	20.1 5.25(1H) (Ha); 1.2(1H) (Hb)	Bicyclic nitroxide 18b
	a	-60	11.5	Dialkyl nitroxide 20
	b ⁺	-30	20.0 5.25(1H) (Ha); 1.25(1H) (Hb)	Bicyclic nitroxide 18b
15c	a	-60	11	Dialkyl nitroxide 20
	b	-30 to -10	30.5	Iminoxyl 16c
			32.0	
	b	-10 to +10	19.75 5.25(1H) (Ha); 0.9(4H) (Hb,Me)	Bicyclic nitroxide 18c
15d	a	-70	30.75	Iminoxyl 16d
	a	-10	11.8	Dialkyl nitroxide 20
	b	0	30.75	Iminoxyl 16d
15e	a	-50	31.0	Iminoxyl 16e
	a	10	12.0	Dialkyl nitroxide 20
	b	-50	31.0	Iminoxyl 16e

^a Method of oxidation. a, treatment with lead tetra-acetate; b, photolysis in di-*t*-butyl peroxide; +, $g=2.0069(3)$.

faded with increasing temperature and at room temperature the solution was shown to contain the diphenylindazole 12a. More efficient conversion into the indazole 12a was achieved by treatment of the oxime with lead tetra-acetate or di-*t*-butyl peroxalate (source of *t*-butoxyl) at or above room temperature when evolution of nitrogen dioxide ($\text{NO} + \text{O}_2$) was obvious. *o*-Phenylazoacetophenone oxime 9b behaved similarly. Product formation is rationalised by the sequence $10 \rightarrow 11 \rightarrow 12$ which includes a favourable 5-exo trigonal cyclisation.⁷ Cyclisation of the oximes 9a and 9b to the indazoles 12a and 12b was also achieved by reaction with acid. Clearly, iminoxyls 10 do not mediate in this cyclisation and an alternative sequence $9 \rightarrow 13 \rightarrow 14 \rightarrow 12$ involving final elimination of nitroxyl (HNO) is postulated.

o-Alkenylphenylmethyleneiminoxyls. Continuous photolysis of a solution of the oxime 15a in di-*t*-butyl peroxide in an ESR spectrometer did not give the spectrum of the corresponding iminoxyl ($a_N \sim 30$ G). Instead, at -40°C a triplet of double doublets [$a_N = 19.75$, $a_H = 5.4(1\text{H})$, $a_H = 1.2$ G(1H), $g = 2.0069$] was detected. A nearly identical spectrum was obtained from the phenyl analogue 15b. Even more interesting was the result with 15c. From -30 to -10°C overlapping spectra of two iminoxyls (a_N 30.0 and 32 G) were present. From -10 to $+10^\circ\text{C}$ these signals were gradually replaced by another spectrum which had $a_N = 19.75$, $a_H = 5.25(1\text{H})$, $a_H = 0.9$ G (4H). Above 20°C only the latter spectrum persisted. The other two oximes listed in Table 1 only gave spectra of the corresponding iminoxyls.

Fig. 1. Spectrum obtained by oxidation of oxime 15a with lead tetra-acetate at -60°C .

When lead tetra-acetate was used as oxidant the spectrum of either the iminoxyl ($a_N \sim 30$ G) or that of the radical with $a_N \sim 20$ G was detected but not both. These spectra were usually accompanied by a second spectrum with $a_N \sim 11-12$ G which usually intensified with increasing temperature as the iminoxyl decayed.

The iminoxyl spectra were similar to that observed from *o*-ethylphenyl phenylmethylene-iminoxyl and are not remarkable. Also, nitroxides with $a_N = 11-12$ G are often detected when oximes are treated with lead tetraacetate and are attributed⁸ to di-*t*-alkyl nitroxides 20 formed from the corresponding nitroso-acetates 19. The spectra with $a_N \sim 20$ G are more interesting and probably arise from the corresponding iminoxyls since in all but one case they are not detected when spectra of the iminoxyl appear and *vice versa*. Exceptionally, with

Scheme 4. 15a–18a, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Bu}^t$; 15b–18b, $\text{R}^1 = \text{R}^2 = \text{Ph}$; 15c–18c, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$; 15d, $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{Bu}^t$; 15e, $\text{R}^1 = \text{Pr}^i$, $\text{R}^2 = \text{Bu}^t$.

15c when both were detected that with $a_N \sim 20$ G intensified as the iminoxyl spectrum faded. Since no spectra with $a_N \sim 20$ G were detected when aryl methylene oximes with saturated *ortho*-alkyl substituents were oxidised we consider that such spectra arise from radicals formed by cycloaddition of the iminoxyl onto the adjacent double bond. However, 5- and 6-membered cyclic dialkyl nitroxides⁹ such as 21 and 22 have a_N values (14–16 G) significantly smaller than 20 G. Indeed, only bicyclic nitroxides have a_N values in this range,⁹ e.g. nitroxide 23¹⁰ has $a_N = 19.8$, $a_H = 5.6(2H)$ and $a_H = 1.4$ G (4H). Hence, we suggest that the iminoxyls undergo 5-exo-trigonal cyclisation followed by intramolecular spin trapping of the ensuing alkyl radicals 17 by the nitron group to give the bicyclic nitroxides 18 whose coupling constants are very similar to those of 23. It is known¹¹ that exo-intramolecular addition is kinetically more favourable than endo addition for such cyclisations and that spin trapping of alkyl radicals by nitrones is fast.¹² However, we cannot satisfactorily account for our failure to detect bicyclic nitroxides from 15d and 15e. Preliminary product studies using lead tetra-acetate as oxidant and the oxime 15a showed (TLC) that many products are formed but none is major.

Methyl-*o*-phenylphenylmethyleneiminoxyl. Oxidation of the oxime 24 with lead tetra-acetate gave 6-methylphenanthridine 27 and its *N*-oxide 26 in low yield. The latter is the expected product of cyclisation of the iminoxyl 25 but 27 is not derived from 26 by reaction with lead tetra-acetate. Previ-

ously,² we produced 27 by cyclisation of the corresponding iminyl but we would not expect iminyls to mediate in the above oxidation. The ESR spectrum of the iminoxyl 25 [$a_N = 32$, $a_H = 1.5$ G (1H)] was detected on reaction of the oxime 24 with lead tetra-acetate at room temperature in the ESR spectrometer. However, this rapidly faded leaving a strong signal due to a di-*t*-alkyl nitroxide ($a_N = 11.75$ G) presumably due to a radical of type 20.

Aryl vinylmethylene iminoxyls. Since we had already shown² that iminyls derived from oximes such as 28a and 28b (Scheme 5) readily cyclised to

Scheme 5. 28a–31a, Ar = Ph; 28b–31b, Ar = *o*-MeC₆H₄.

give quinolines we reasoned that iminoxyls might behave similarly. Hence, photolysis of the oxime 28b in the ESR cavity gave an intense spectrum of a radical with $a_N = 7.15$, $a_H = 2.75$ (3H) and $a_H = 0.90$ G (2H). A very similar spectrum was obtained when the oxime in dichloromethane was treated with lead tetra-acetate at -60°C but this faded as the temperature was increased. The related oxime 28a behaved similarly on photolysis in di-*t*-butyl peroxide but with lead tetra-acetate mixed spectra were produced which changed with temperature and so were difficult to interpret. Iminoxyls were not detected under any of the sets of conditions used although with oximes 32 and 33 iminoxyl spectra (a_N 30 G) were detected without difficulty. Hence, it appears that the iminoxyls 29 are undergoing a reaction not available to iminoxyls derived from 32 and 33. In view of our previous findings² that iminyls derived from oximes 28a and 28b cyclised to give quinolines but those from 32 and 33 did not, we believe that iminoxyls 28a and 28b are behaving similarly. The product radicals detected are most

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likely to be the nitroxides **31a** and **31b** ($a_{4-H} = a_{6-H} = a_{8-H}$) indicated. However, when oxime **28b** was oxidised with nickel peroxide or with lead tetra-acetate on a preparative scale the quinoline *N*-oxide **34** was not detected in the complex product mixtures.

Iminoxyls are known¹³ to dimerise and couple with other radicals but addition to multiple bonds and aryl rings has not previously been observed.

EXPERIMENTAL

IR spectra were measured as KBr discs and NMR spectra in deuteriochloroform unless stated otherwise. Merck GF₂₅₄ silica was used for chromatographic separations.

o-(Phenylazo)benzophenone **9a**. Aniline (0.31 g, 3.5 mmol) was added dropwise to a solution of *o*-nitrosobenzophenone¹⁴ (0.74 g, 3.5 mmol) in acetic acid (10 ml) and the mixture was stirred for 18 h. Ether was added and the ethereal solution was washed with 2 M sodium hydroxide, water, and dried. Removal of solvent left the crude product as a red oil which was purified by PLC using dichloromethane as eluant to give *o*-phenylazobenzophenone (57%), m.p. 56–57°C (from hexane) [I.R. 1670 cm⁻¹. Anal. C₁₉H₁₄N₂O]. *o*-Phenylazobenzophenone did not react with (a) hydroxylamine hydrochloride in aqueous alcohol under reflux for 4 h; (b) amino-oxyacetic acid hemihydrochloride in aqueous ethanol under reflux for 3 h nor in a sealed vessel at 90°C for 9 h; (c) methoxyamine hydrochloride in aqueous alcohol under reflux for 3 h nor in a sealed vessel at 90°C for 5 h.

o-Methylazoxybenzophenone **1e** was prepared by the literature method.⁴ It did not react with hydroxylamine hydrochloride in aqueous alcohol under reflux for 5 h.

o-Aminoacetophenone oxime¹⁵ **5a** and *o*-aminobenzophenone oxime,¹⁶ were obtained from the corresponding aminoketones by reaction with hydroxylamine in the usual way.

o-Phenylazoketoximes **9**. A solution of the *o*-aminoketoxime (0.015 mol) and nitrosobenzene (0.015 mol) in acetic acid (50 ml) was stirred at room temperature for 17 h. Ether was added and the solution was washed with 2 M sodium hydroxide, water, and dried. Removal of solvent left the crude

product *o*-(phenylazo)acetophenone oxime **9a** (64%) which gave orange needles, m.p. 134.5–136.5°C (from ether–hexane) [¹H NMR: 2.33 (3H, s), *ca.* 7.55 (9H, s). IR 3220 cm⁻¹. Anal. C₁₄H₁₃N₃O]. *o*-(Phenylazo)benzophenone oxime was purified by chromatography (column) using ether as eluant. It formed fine orange needles, m.p. 147–150°C (from ether–hexane) [IR 3220 cm⁻¹. Anal. C₁₉H₁₅N₃O].

Methyl(o-phenylazo)phenylmethyleamino-oxyacetic acids **3**. Bromoacetic acid (2.1 g, 0.015 mol) and sodium hydroxide (1.24 g, 0.03 mol) were added to a solution of the *o*-(phenylazo)ketoxime (0.01 mol) in water (50 ml) and ethanol (25 ml). The mixture was heated under reflux for 21 h. Ethanol was removed *in vacuo* and the aqueous residue was acidified with hydrochloric acid. The acid solution was extracted with ether and the ether was extracted with aqueous bicarbonate solution. After acidification this was extracted with chloroform. Evaporation of the dried extracts and crystallisation of the residue gave the product. *o*-(Phenylazo)acetophenone oxime gave *methyl(o-phenylazo)phenylmethyleamino-oxyacetic acid* (51%), as red needles from ether–hexane, m.p. 140–141.5°C [¹H NMR: 2.4 (3H, s), 4.47 and 4.75 (2 H, both s), 7.38–7.95 (9H, m). IR 3440–2570, 1720, 1705 cm⁻¹. Anal. C₁₆H₁₅N₃O₃]. *o*-(Phenylazo)benzophenone oxime gave *phenyl(o-phenylazo)phenylmethyleamino-oxyacetic acid* (42%) as orange needles from chloroform–hexane, m.p. 163–165°C [¹H NMR: 4.6 and 4.8 (2H, both s), 7.1–7.6 (14H, m). IR 3410, 1730, 1700 cm⁻¹. Anal. C₂₁H₁₇N₃O₃].

Oxidation of these two acids with persulfate in aqueous solution, as previously described,^{1–3} gave complex product mixtures in which the indazoles **12a** and **12b** were the only identifiable products.

Reactions of o-(phenylazo)acetophenone oxime **9b**. (a) *With acid*. To a solution of the oxime in chloroform a few drops of acetic acid or 2 M hydrochloric were added and the solution was left for 15 min when the colour faded. The solution was washed with aqueous bicarbonate solution, dried, and evaporated. Crystallisation of the residue from hexane gave 3-methyl-2-phenyl-2*H*-indazole **12b**.

(b) *With di-*t*-butyl peroxalate*. The peroxalate (23 mg) was added to a solution of the oxime (48 mg) in benzene. After 10 min the colourless solution was evaporated and the residue crystallised as before to give the indazole **12b** quantitatively. A similar

result was obtained when crystals of lead tetraacetate (free from acetic acid) were added to a solution of the oxime **9b** in benzene.

Reactions of *o*-(phenylazo)benzophenone oxime **9a.** This oxime reacted with lead tetraacetate and di-*t*-butyl peroxalate as described for **9b** to give 2,3-diphenyl-2H-indazole.⁵

Oxidation of 1,2-dihydro-4-methyl-2-phenylquinazoline 3-oxide **6b.** Lead tetraacetate (0.96 g) (free from acetic acid) was added to a solution of the quinazoline 3-oxide (0.48 g) in benzene (30 ml) and the mixture was stirred at room temperature for 3 h. The yellow brown solid remaining after removal of solvent was chromatographed (PLC) using dichloromethane ethyl acetate (9:1) as eluant to give pale yellow needles of 4-methyl-2-phenylquinazoline 3-oxide (60%) **8b**.

Similar treatment of 1,2-dihydro-2,4-diphenylquinazoline 3-oxide **6a** gave 2,4-diphenylquinazoline 3-oxide **8a**.

Bromo-alkenes. The following new bromoalkenes were prepared by a previously described method.¹ *o*-(1'-Butenyl)bromobenzene was an oil (b.p. 82–84 °C/0.4 kPa). [MS Mol. wt., obs. 210.0042, calc. for C₁₀H₁₁⁷⁹Br 210.0045. ¹H NMR: 1.05 (3H, t), 2.2 (2H, q, *J* 2 Hz), 6.15 (1H, dt, *J* 5 Hz and 2 Hz), 6.67 (1H, d, *J* 5 Hz), 6.98 (1H, t, *J* 2 Hz), 7.18 (1H, t, *J* 2 Hz), 7.45 (2H, dd, *J* 2 Hz)]. *o*-(3'-Methyl-1'-butenyl)bromobenzene was a thick oil [MS Mol. wt. obs. 224.0200, calc. for C₁₁H₁₃⁷⁹Br 224.0201. ¹H NMR: 1.08 (6H, d, *J* 2 Hz), 2.5 (1H, oct, *J* 2 Hz), 6.12 (1H, dd, *J* 5 Hz and 2 Hz), 6.68 (1H, d, *J* 5 Hz), 7.04 (1H, t, *J* 2 Hz), 7.23 (1H, t, *J* 2 Hz), 7.5 (2H, dd, *J* 2 Hz)].

Preparation of *o*-vinylketoximes **15. General.** 1.6M Butyl-lithium (20 m, 0.032 mol) was added to a solution of the bromoalkene (0.013 mol) in ether under nitrogen, and the mixture was stirred at room temperature for 5 h. A solution of pivalonitrile (2.49 g, 0.03 mol) in ether was added dropwise and the mixture was then heated under reflux for 15 min. Ethanol (37.5 ml), acetic acid (1.5 ml) and hydroxylamine hydrochloride (1.75 g, 0.025 mol) were added and the mixture was heated under reflux for 5 h. After cooling, water (65 ml) was added and the ethanol was removed *in vacuo*. The aqueous solution was extracted with ether and the extracts were washed with water and dried. Removal of solvent left the crude oxime. *t*-Butyl *o*-styrylphenyl ketoxime **15a** formed rhombs, m.p. 166–169 °C (from chloroform) [¹H NMR: 1.17 (9H, s), 6.94–7.55 (11H, m). IR: 3240 cm⁻¹. Anal. C₁₉H₂₁NO]. *t*-Butyl-*o*-(1'-butenyl)phenyl ketoxime **15d** gave plates, m.p. 122–124 °C (from hexane) [¹H NMR 1.02 (3H, t), 1.12 (9H, s), 2.17 (m, CH₂), 6.23 (2H, s), 6.95–7.6 (4H, m). IR: 3410 cm⁻¹. Anal. C₁₅H₂₁NO]. *t*-Butyl *o*-(3'-methyl-1'-butenyl)-phenyl ketoxime **15e** formed plates, m.p. 106–109 °C (from chloroform–hexane)

[¹H NMR: 1.08 (6H, d, *J* 7 Hz), 1.15 (9H, s), *ca.* 2.4 (1H, m), 6.19 and 6.27 (2H, both s), 7.05–7.75 (4H, m). IR: 3280 cm⁻¹. Anal. C₁₆H₂₃NO].

The oximes **15b** and **15c**, **28a**, **28b**, **24**, **32** and **33** were prepared by the literature methods.^{1,2,18}

Oxidation of *o*-phenylacetophenone oxime. Lead tetraacetate (0.98 g, 2.2 mmol) (free of acetic acid) was added to a solution of *o*-phenylacetophenone oxime (0.42 g, 2.0 mmol) in benzene and the mixture was stirred at room temperature for 2 h. The solid was collected and the filtrate was evaporated to dryness. The residue was chromatographed (PLC) using ethyl acetate–dichloromethane (1:19) as eluant giving 6-methylphenanthridine¹⁸ (12%) and 6-methylphenanthridine *N*-oxide¹⁹ (20%).

ESR measurements. ESR spectra were recorded on an E104A Varian spectrometer. The samples were prepared as follows.

(a) A solution of the oxime in dichloromethane was degassed and then cooled to –90 °C in the cavity of the spectrometer. One crystal of lead tetraacetate, which had previously been freed from acetic acid by washing with dichloromethane, was then added. Spectra were recorded at regular intervals between –90 °C and room temperature.

(b) A degassed solution of the oxime in di-*t*-butyl peroxide was photolysed (1 kW Hg-vapour lamp) in the cavity of the spectrometer. Spectra were recorded between –60 °C and room temperature.

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