Thermal and photochemical reactivity of β,γ-unsaturated oximes in the presence of $SnCl_4$

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Dedicated to Dr. Douglas Lloyd on the occasion of his 80th birthday

Abstract

The thermal reaction of some symmetrically substituted β,γ-unsaturated oximes 2a-d in the presence of one equivalent of tin tetrachloride in toluene leads to the formation of 5,6-dihydro-4*H*-1,2-oxazines 3a-d. The photochemical reaction follows a different path and yields 5-(diarylhydroxymethyl)-4,4-dimethyl-4,5-dihydroisoxazoles 6a, b. A cationic mechanism is proposed for the thermal cyclisation while the photochemical process is thought to involve an SET process.

Keywords: Dihydrooxazines, dihydroisoxazoles, oximes, cyclisation, carbocations, photochemistry, SET

Introduction

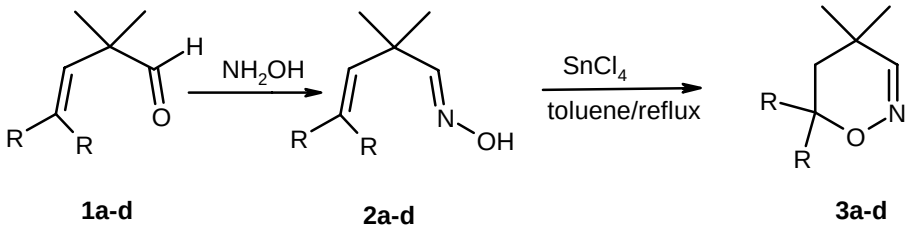
β,γ-Unsaturated oximes and their derivatives have provided a fruitful area of study over the past two decades. Our own recent studies have recorded[1] the photochemical cyclisation of such oximes under SET conditions using DCA and also a novel oxidative intramolecular cyclisation to yield *peri*-naphthisoxazoles.[2] However, the definitive earlier work by Armesto and his co-workers[3] demonstrated the usefulness of the photochemical reactions of such species in the discovery and subsequent study and development of the aza-di-π-methane rearrangement. In another account Armesto *et al.*[4] reported the photochemical transformations of some β,γ-unsaturated oximes in the presence of BF_3 etherate whereby a new reaction, the formation of dihydroisoxazoles, was observed. Subsequent to that study there have been few, if any, other reports of the reactivity of such systems in the presence of Lewis acid catalysts. Thus, it was of interest to investigate the thermal and photochemical reactivity of some of these oximes with

another Lewis acid. In this paper we described thermal and photochemical examples of the reactivity of the oximes in the presence of $SnCl_4$.

Results and Discussion

The aldehydes **1a-d** required for the synthesis of the oximes **2a-d** were readily prepared using a slight modification of the procedure developed by Zimmerman and Pratt.[5] The oximes **2a-d** were synthesized by conventional means using the method described earlier by Armesto and his co-workers.[6]

The thermal reaction of the β,γ-unsaturated oximes **2a-d** in the presence of stoichiometric amounts of tin tetrachloride was investigated. The procedure adopted involved reaction of the unsaturated oxime **2a** (0.66 mmol) at reflux in toluene (35 ml) with one equivalent of tin tetrachloride for about 20 h. The solution was allowed to cool to room temperature and poured into water (50 ml). Conventional work-up gave a semi-solid residue TLC analysis of which showed the presence of a new compound. This was isolated by conventional column chromatography (toluene/ethyl acetate 7:1). The isolated product exhibited ^{1}H NMR signals as singlets at δ 7.00 for an oximino hydrogen and at δ 2.65 for a methylene group. These resonances justify the assignment of the structure of the new product as the dihydrooxazine **3a**. The others oximes **2c-d** behaved similarly affording the dihydrooxazines **3c-d** (Scheme 1). The yields of these new compounds are shown in the table.



1a-d **2a-d** **3a-d**

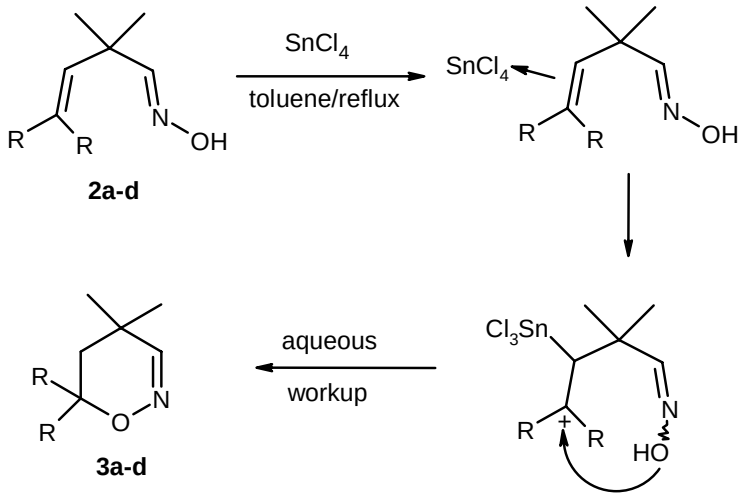
Scheme 1

Table1. Conditions used and yields of dihydrooxazines formed

Oxime	R	time	Dihydrooxazine	Oxime recovered
2a	C_6H_5	19h	**3a**, 35%	**2a**, 14%
2b	*p*-Pr^{i}C$_6$H$_4$	17h	**3b**, 47%	-
2c	*p*-Bu^{t}C$_6$H$_4$	18h	**3c**, 57%	**2c**, 16%
2d	CH_3CH_2	18h	**3d**, 46%	-

There are a few methods[7-9] described in the literature for the preparation of 5,6-dihydro-4*H*-1,2-oxazine derivatives. For example, Brandman and Conley[7] described the formation of 3-methyl-4*H*-5,6-dihydro-1,2-oxazine in moderate yield by treatment of 5-chloro-2-pentanone with hydroxylamine hydrochloride in the presence of potassium carbonate while Zimmer and Reissig[8] used a hetero-Diels-Alder reaction between 1,1,1-trifluoro-2-nitroso-2-propene and electron-rich alkenes. In an earlier study Thoai *et al.*[9] described the formation of dihydro-1,2-isoxazoles by treatment of α,β-unsaturated oximes with sulphuric acid. Presumably, the oxime isomerises in the first step to the β,γ-unsaturated oxime and then cyclisation leads to the product. Under these conditions they[9] also obtained low yields of 5,6-dihydro-4*H*-1,2-oxazines. Our method seems to provide a more general route to these latter compounds.

The fact that dihydrooxazines are obtained from the thermal reaction of the oximes suggests that the most likely mechanism of cyclisation involves a cationic intermediate. The formation of carbocations by tin(IV) tetrachloride is well known.[10, 11] Thus, we suggest that tin tetrachloride behaves as a Lewis acid and complexes with the alkene double bond. This could involve the formation of a tin–carbon σ-bond and results in the production of a stabilized cation. For compounds **2a-d** the resultant cation centre will be at C4 where it is stabilized by two aryl groups in **2a-c** and by two alkyl groups in **2d**. Cyclisation takes place by attack of the hydroxyl group of the oxime moiety. After the cyclisation step aqueous hydrolysis of the complex gives the final products **3a-d** (Scheme 2).

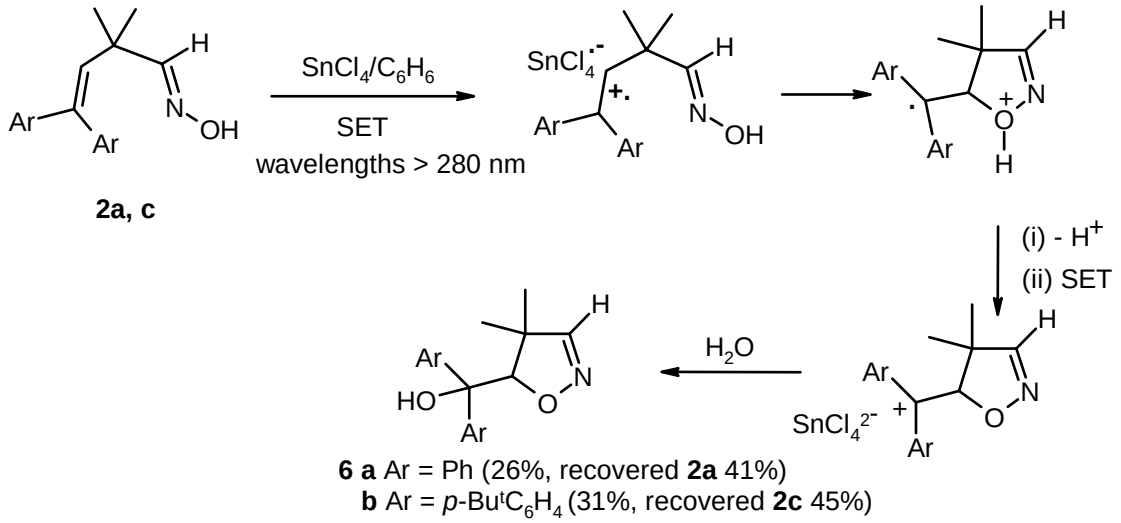


Scheme 2

The involvement of a stabilized carbocation has support from the outcome of the thermal cyclisation of oxime **4** under the same conditions as those used above. In this instance the phenyl group at C3 will stabilize the cation centre. This postulate is confirmed by the isolation, in low yield, of a compound identified as the dihydroisoxazole **5**.

4 **5**

Clearly, the thermal cyclisation of the 4,4-disubstituted oximes affording dihydrooxazines is different to the reaction observed in the photochemical transformation of oxime **2a** in the presence of BF_3 etherate. Under these conditions **2a** is trnasformed into the dihydroisoxazole **6a.**. In view of this disparity it was important to establish if irradiation in the presence of $SnCl_4$ followed the same path to a dihydroisoxazole. Irradiation using the conditions described in the experimental did give the same dihydroisoxazole **6a** in a similar yield to that reported[4] in the earlier study. The same cyclisation mode was observed for oxime **2c** that gave the dihydroisoxazole **6b**. It is tempting to assume that the reactions observed with $SnCl_4$ follows a Single Electron Transfer (SET) mechanism. In the example with BF_3 etherate it was assumed that the Lewis acid complexed with the oximino group. However, with $SnCl_4$ it seems likely that the complex formed with the Lewis acid involves the double bond. This has precedence in the thermal reactions. A possible mechanism that accounts for the formation of the dihydroisoxazoles under the conditions used here is shown in Scheme 3.



Scheme 3

It seems logical that the formation of the hydroxylated products must involve the formation of a cation centre at the diarylmethyl site as shown in Scheme 3.

Conclusions

The experiments described above show that dihydrooxazines can be synthesized readily in reasonable yields by the use of $SnCl_4$ under thermal conditions. The cyclisations are readily accounted for by a cationic mechanism. When the oxime/$SnCl_4$ mixture in benzene is irradiated a different reaction path is followed and involves a SET. This cyclisation yields dihydroisoxazole derivatives.

Experimental Section

General Procedures. IR spectra were recorded on a Nicolet 205 spectrophotometer and UV/VIS spectra on a Perkin-Elmer Lambda 16 spectrometer. ^1H and ^{13}C NMR spectra ($CDCl_3$ as solvent and TMS as internal standard) were recorded on a Bruker AM-200 at 200 MHz and 50 MHz, respectively. Mass spectra were recorded on a VG 70-S spectrometer using Datasystem 11-250J. Elemental analyses were carried out on a Carlo Erba Model 1106. Melting points were measured on an Electrothermal apparatus and are uncorrected. TLC was carried out on glass plates using Silica gel 60 F_{254} (Merck).

Synthesis of enals 1a-d. Enal **1a** was synthesised by a modification of the method described by Zimmerman and Pratt.[5] The other enals **1c-d** were obtained by the same method.

4,4-Di-(*p*-isopropylphenyl)-2,2-dimethylbut-3-enal (1b). This was obtained in 74% yield as an orange oil; $\nu_{max.}$ ($CDCl_3$): 1720 (C=O), 1600 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.2 (1H, s, CHO), 7.3-6.9 (8H, m, aromatic H), 6.0 (1H, s, vinyl H), 2.92 (2H, m, C<u>H</u>$(CH_3)_2$), 1.4-1.0 (18H, m, 6 x CH_3).

4,4-Di-(*p*-*tert*-butylphenyl)-2,2-dimethylbut-3-enal (1c). This was obtained in 41 % as an orange oil; $\nu_{max.}$ ($CDCl_3$): 1750 (C=O), 1600 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.2 (1H, s, CHO), 7.4-7.1 (8H, m, aromatic H), 6.0 (1H, s, vinyl H), 1.2 (24H, m, 8 x CH_3).

4,4-Diethyl-2,2-dimethylbut-3-enal (1d). This was obtained in 98 % yield as a yellow oil; $\nu_{max.}$ ($CDCl_3$): 1750 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.35 (1H, s, CHO), 4.95 (1H, s, vinyl H), 2.0-1.7 (4H, m, 2 x CH_2), 1.1 (6H, m, 2 x CH_3), 0.9 - 0.8 (6H, m, 2 x CH_3).

Synthesis of oximes

The general synthesis of the oximes was carried out as described by Armesto and his co-workers.[6] Thus, 13.7 mmol of the enal was reacted with 20.0 mmol of hydroxylamine hydrochloride in pyridine (3 ml) and ethanol (60 ml). The mixture was heated at reflux for 4 h. The oxime was obtained following work-up and column chromatography using diethyl ether/hexane gradient elution.

4,4-Diphenyl-2,2-dimethylbut-3-enal oxime (2a). m.p.: 69-71 ^oC (lit.[4] m.p.: 69-70 ^oC).

4,4-Di-(*p*-*iso*propylphenyl)-2,2-dimethylbut-3-enal oxime (2b). Crystallized from hexane to give (3.2 g, 67%) as white needles; m.p.: 128-129 ^oC; $\nu_{max.}$ (KBr): 3420 (OH), 1620 (C=N), 1600 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.55 (1H, s, OH), 7.3-6.9 (8H, m, aromatic H), 6.9 (1H, s, CH=N), 5.95 (1H, s, vinyl), 2.9-2.8 (2H, m, 2 x CH), 1.25-1.1 (18H, s, 6 x CH_3); δ_C ($CDCl_3$): 157.5 (C=N), 147.9-126.0 (aromatic C and C=C), 39.3 (<u>C</u>$(CH_3)_2$), 33.9 (CH), 33.7 (CH), 27.5 (2 x CH_3), 24.0 (4 x CH_3); $\lambda_{max.}$ (cyclohexane): 255 nm (0.85), 238 nm (0.9) and 210 nm (1.9); MS: m/z (%) 349 (M^+, 72%), 332 (100), 264 (33), 217 (13), 162 (33), 113 (18); Anal. Calcd. for $C_{24}H_{31}NO$: C, 82.47; H, 8.94; N, 4.00. Found: C, 83.72; H, 9.12; N, 3.76.

4,4-Di-(*p*-*tert*-butylphenyl)-2,2-dimethylbut-3-enal oxime (2c). Obtained as white needles (0.9 g, 31%); m.p.: 130-132 ^oC; $\nu_{max.}$ (KBr): 3300 (OH), 1620 (C=N), 1600 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.0 (1H, s, OH), 7.4-7.0 (8H, m, aromatic H), 7.0 (1H, s, CH=N), 6.0 (1H, s, vinyl H), 1.3 (9H, s, 3 x CH_3), 1.3 (9H, s, 3 x CH_3), 1.15 (6H, s, 2 x CH_3); δ_C ($CDCl_3$) 163.2 (C=N), 151.6-127.6 (aromatic C and C=C), 39.3 (<u>C</u>$(CH_3)_2$), 34.5 (2 x Ph<u>C</u>$(CH_3)_3$), 31.4 (9 x CH_3), 26.0 (2 x CH_3); $\lambda_{max.}$ (EtOH): 247 nm (0,32) and 203 nm (0.81); MS: *m/z* (%) 377 (M^+, 36%) 360 (100), 348 (56), 330 (16), 304 (60), 275 (44), 219 (24), 161 (30), 132 (30), 91 (16); Anal. calcd. for $C_{26}H_{35}NO$: C, 82.71; H, 9.34; N, 3.71%. Found: C, 82.01; H, 9.28; N, 3.41.

4,4-Diethyl-2,2-dimethylbut-3-enal oxime (2d). Obtained as a colourless oil in 80 % yield; ν_{max} (film): 3300 (OH), 1640 (CN) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 8.65 (1H, s, OH), 7.38 (1H, s, CH=N), 5.03 (1H, s, vinyl H), 2.1 - 0.9 (4H, m, 2 x CH_2), 1.2 (6H, s, 2 x CH_3), 1.0 - 0.9 (6H, m, 2 x CH_3); ^{13}C NMR ($CDCl_3$): δ 158.6 (C=N), 145.9 and 128.1 (C=C), 37.6 ($\underline{C}(CH_3)_2$), 28.4 (CH_2), 27.6 (2 x CH_3), 23.1 (CH_2), 13.0 and 12.8 (2 x CH_3 from ethyl); MS: *m/z* (%)169 (M^+ 9), 154 (100), 140 (48), 122 (22), 108 (15), 95 (16), 83 (11), 69 (31). (Found: M^+, 169.1456. $C_{10}H_{19}NO$ requires M^+, 169.1466).

3-Phenyl-2,2-dimethylbut-3-enal oxime (4). This was synthesized by the method of Armesto and co-workers[12] and was obtained in 70% yield as a pale yellow oil showing the following spectral characteristics; $\nu_{max.}$ (film): 3300 (OH), 1620 (C=N), 1600 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.1 (1H, s, OH), 7.5 (1H, s, CH=N), 7.4-7.0 (5H, m, aromatic H), 5.2 (1H, s, vinyl H), 5.0 (1H, s, vinyl H), 1.3 (6H, s, 2 x CH_3); ^{13}C NMR ($CDCl_3$): δ 153 (C=N), 141.6-114.3 (aromatic C and C=C), 47.7 ($\underline{C}(CH_3)_2$), 25.7 (2 x CH_3); $\lambda_{max.}$ (cyclohexane): 254 (0.4) and 210 nm (1.4); MS: m/z (%) 189 (M^+, 12%): 175 (28), 174 (100), 157 (23), 156 (16), 135 (47), 129, (16), 128 (15), 115 (15); (Found: M^+, 189.1151. $C_{12}H_{15}NO$ requires M, 189.1154).

General reaction conditions for the thermal reactions

A solution of 0.94 mmol. of the oxime and 1.32 mmol. $SnCl_4$ in 35 ml toluene was refluxed for 19 hours. After aqueous work-up and column chromatography using elution with toluene/ethyl acetate (7:1) the dihydrooxazine and starting material were obtained.

6,6-Diphenyl-5,6-dihydro-4,4-dimethyl-4*H*-1,2-oxazine (3a). 96 mg (35 %) of the dihydrooxazine derivative **3a** and 36 mg (14 %) of the starting material **2a** was obtained. Dihydrooxazine **3a** was re-crystallized from cyclohexane; m.p.: 137 °C; ^{1} H NMR (CDCl3): δ 7.40 - 7.10 (10H, m, Ph-H), 7.00 (1H, s, CH=N), 2.65 (2H, s, CH2), 0.80 (6H, s, 2 x CH3); ^{13}C NMR (CDCl3): δ 157.0 (C=N), 143.3 - 1126.4 (aromatic C), 80.9 (C-O), 42.5 (CH2), 28.3 (2 x CH3); $\nu_{max.}$ (KBr): 1620 (C=N) cm-1; MS: *m/z* (%) 265 (M+ 35), 236 (18), 180 (100), 165 (28); Anal. calcd. for $C_{18}H_{19}NO$ (265.4): C 81.48; H 7.22; N 5.28. Found: C 81.24; H 7.30; N 5.47.

6,6-Di-(*p*-*iso*propylphenyl)-5,6-dihydro-4,4-dimethyl dihydrooxazine (3b). Obtained in 47% yield m.p.: 141 °C (recrystallised from cyclohexane); ν_{max} (KBr): 1620 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.3 (4H, d, J = 9 Hz, aromatic H), 7.15 (4H, d, J = 9 Hz, aromatic H), 6.95 (1H, s, CH=N), 2.85 (2H, m, 2 x CH), 2.68 (2H, s, CH_2), 1.2 (6H, s, 2 x CH_3), 1.15 (6H, s, 2 x CH_3), 0.8 (6H, s, 2 x CH_3); ^{13}C NMR ($CDCl_3$): δ 156.9 (C=N), 147.7 - 126.7 (aromatic C), 80.9 (C-O), 42.7 (CH_2), 33.7 (2 x CH), 28.3 (2 x CH_3), 24.0 (4 x CH_3); MS: *m/z* (%) 349 (M^+ 24), 320 (15), 264 (100), 249 (39), 145 (12); Anal. calcd. for $C_{24}H_{31}NO$ (349.5): C 82.48; H 8.94; N 4.00. Found: C 82.51; H 8.97; N 3.88.

6,6-Di-(*p*-*tert*-butylphenyl)-5,6-dihydro-4,4-dimethyl dihydrooxazine (3c). Obtained in 57 % yield accompanied by recovered starting material **3c** (16%). The dihydrooxazine **3c** was recrystallised from cyclohexane; m.p.: 229 °C ν_{max} (KBr): 1620 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$):

δ 7.4 (8H, m, aromatic H), 7.05 (1H, s, CH=N), 2.7 (2H, s, CH_2), 1.3 (18H, s, 6 x CH_3), 0.8 (6H, s, 2 x CH_3); ^{13}C NMR ($CDCl_3$): δ 156.9 (C=N), 150.0 - 125.1 (aromatic C), 80.6 (C-O), 42.8 (CH_2), 34.4 ($\underline{C}(CH_3)_9$), 31.3 (6 x CH_3), 28.3 (2 x CH_3); MS: *m/z* (%) 377 (M^+ 30), 360 (17), 348 (22), 292 (100), 277 (93), 57 (28); Anal. calcd. for $C_{26}H_{35}NO$ (377.5): C 82.71; H 9.35; N 3.71. Found: C 82.68; H 9.34; N 3.60.

6,6-Diethyl-4,4-dimethyl dihydrooxazine (3d). Obtained in 46 % yield as an oil; ν_{max} (film): 1650 (C=N) cm^{-1}: ^{1}H NMR ($CDCl_3$): δ 7.0 (1H, s, CH=N), 1.65 (2H, s, CH_2), 1.6 - 1.3 (4H, m, 2 x CH_2), 1.1 (6H, s, 2 x CH_3), 0.9 (6H, t, J = 7.4 Hz, 2 x CH_3): ^{13}C NMR ($CDCl_3$): δ 158.0 (C=N), 80.0 (C-O), 40.7 (CH_2), 31.3 (2 x CH_2), 27.8 ($\underline{C}(CH_3)_2$), 27.8 (2 x CH_3), 7.6 (2 x CH_3): MS: *m/z* (%) 169 (M^+ 2), 154 (34), 140 (50), 124 (20), 109 (13), 95 (24), 85 (24), 83 (20), 69 (30), 57 (100), 55 (82), 53 (15).

4,4,5-Trimethyl-5-phenyl-4,5-dihydroisoxazole (5). After work-up and column chromatography, dihydroisoxazole **5** (31 mg, 12 %) was obtained as an oil. $\nu_{max.}$ (film): 1600 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.4 - 7.1 (5H, m, aromatic H), 6.95 (1H, s, CH=N), 1.5 (3H, s, CH_3), 1.3 (3H, s, CH_3), 0.6 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$): δ 156.6 (C=N), 128.6 - 125.2 (aromatic C), 85.0 (C-O), 42.8 (CH_2), 53.0 ($\underline{C}(CH_3)_2$), 25.4 (CH_3), 23.9 (CH_3), 20.0 (CH_3); MS: *m/z* (%) 190 (M+1 9), 174 (45), 146 (11), 131 (22), 121 (100), 105 (57), 91 (21), 77 (38), 69 (21).

General conditions for irradiation of oximes with $SnCl_4$

In the examples reported 250 mg (0.94 mmol) of the oxime was dissolved in 250 ml benzene and an equivalent amount of $SnCl_4$ (0.94 mmol) was added. The irradiations were carried out in an immersion well apparatus fitted with a Pyrex filter and using a 400 W medium pressure Hg arc lamp. Argon was purged through the solution for 30 min before and during the irradiation. The times of irradiation varied from 0.5 – 3.0 h. The mixtures reactions were quenched in 100 ml water. After conventional work-up the product was isolated by column chromatography using gradient elution with diethyl ether/hexane.

Irradiation of 4,4-diphenyl-2,2-dimethylbut-3-enal oxime (2a).

Irradiated for 3 h. Chromatography gave the dihydroisoxazole **6a** (67 mg, 26 %) and recovered starting material **2a** (84 mg, 41 %).

5-(Diphenylhydroxymethyl)-4,5-dihydro-4,4-dimethyldihydroisoxazole (6a). was recrystallised from cyclohexane. m.p.: 179 °C (lit.[4] m.p.: 179 °C); $\nu_{max.}$ (KBr): 3280 (OH), 1650 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.80 - 7.00 (10H, m, Ph-H), 6.88 (1H, s, CH=N), 5.23 (1H, s, CH), 3.20 (1H, s, OH), 1.10 (6H, s, 2 x CH_3); ^{13}C NMR ($CDCl_3$): δ 158.1 (C=N), 128.4 - 125.5 (aromatic C), 89.1 (C-O), 51.4 ($\underline{C}(CH_3)_3$), 27.7 (CH_3), 20.7 (CH_3); MS: m/z (%) no M^+, 183 (100), 167 (12), 105 (53), 77 (26). The spectral details for this compound were identical to those reported earlier by us.[4]

Irradiation of 4,4-Di-(*p*-*tert*-butylphenyl)-2,2-dimethylbut-3-enal oxime (2c).
The oxime was irradiated for 1 h. Chromatography gave the dihydroisoxazole **6b** (81 mg, 31%) and recovered starting material **2c** (112 mg, 45 %).
5-(Di-*p*-tert-butylphenylhydroxymethyl)-4,5-dihydro-4,4-dimethyldihydroisoxazole (6b). m.p.: 228 - 229 °C (recrystallised from cyclohexane); $\nu_{max.}$ (KBr): 3350 (OH), 1650 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.6 - 7.2 (8H, m, aromatic H), 6.88 (1H, s, CH=N), 5.20 (1H, s, CH), 2.9 (1H, s, OH), 1.3 (18H, m, 6 x CH_3), 1.05 (3H, s, CH_3), 1.0 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$): δ 158.1 (C=N), 149.7 (aromatic C-$C(CH)_3$), 144.1 - 124.7 (aromatic C), 89.5 (C-O), 51.3 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 31.3 (*t*-butyl CH_3), 27.0 (CH_3), 20.8 (CH_3); MS: m/z (%) no M^+, 295 (100), 239 (15), 161 (98), 118 (15), 91 (12); Anal. Calcd. For $C_{26}H_{35}NO_2$: C 79.35; H 8.96; N 3.56; Found: C 79.13; H 8.80; N 3.25.

Acknowledgements

We thank the University of Dundee and the EC (ERBCHRXCT930151) for financial support.

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