Photochemistry of the Carbon–Nitrogen Double Bond. Part 2.[1] An Investigation of the 3-Methylenepropan-1-imine and 3-Oxopropan-1-imine Chromophores

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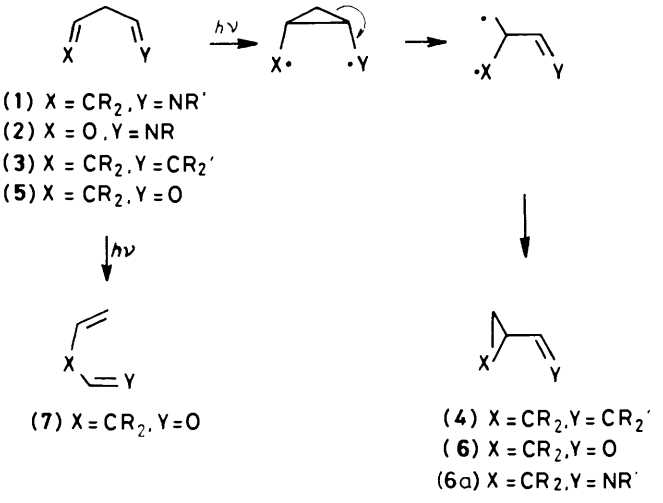
The synthesis of the non-conjugated imino compounds *N*-methoxy-2,2,4-trimethyl-1-phenylpent-3-en-1-imine (**8**), *N*-methoxy-2,2-dimethyl-4,4-diphenylbut-3-en-1-imine (**9**), 2-(1,1-dimethyl-3,3-diphenylprop-2-enyl)-4,4-dimethyl-4,5-dihydro-oxazole (**10**), and 2-benzoyl-*N*-methoxy-2-methylpropan-1-imine (**11**) is described and their photochemistry reported. *cis-trans* Isomerisation was observed for compounds (**8**) and (**11**), the latter also undergoing N–O bond fission to yield 2-benzoyl-2-methylpropiononitrile (**35**). Compound (**9**) formed photoproducts in only trace amounts whereas the dihydro-oxazole (**10**) was photochemically inert.

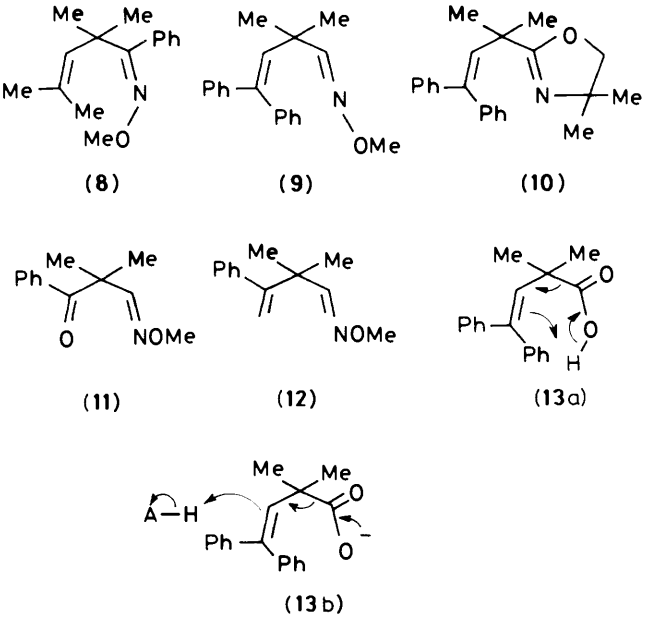
Compounds containing a carbon–nitrogen double bond have been shown to undergo a variety of excited-state reactions including geometrical isomerisation, photoreduction, photocyclisation, cycloaddition, α-cleavage and rearrangement.[2] We have recently reported both carbon–carbon and carbon–nitrogen double bond geometrical isomerisation photoprocesses in an α,β-unsaturated oxime ether.[1]



Scheme 1.

We now report on the photoreactions of some compounds containing a non-conjugated carbon–nitrogen double bond based on the 3-methylene- (**1**) and 3-oxo-propan-1-imine (**2**) chromophores. These systems are of interest because of their analogy to 1,4-dienes, which undergo the Zimmerman di-π-methane rearrangement,[3] (**3**) ⟶ (**4**)(Scheme 1), and to β,γ-unsaturated ketones, which undergo the oxa-di-π-methane rearrangement and/or a 1,3-acyl shift,[3a,4] (**5**) ⟶ (**6**) and (**7**) respectively (Scheme 1). Compounds (**8**), (**9**), and (**10**), configurationally stable aza analogues of 1,4-dienes known[3] to undergo di-π-methane rearrangement, were chosen for investigation. The oxime ether (**11**) was also included in the study.

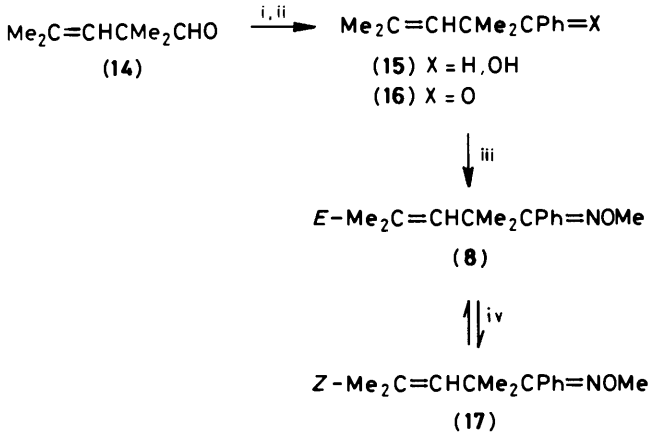
No examples of an aza-di-π-methane rearrangement [Scheme 1, (**1**) ⟶ (**6a**)] were known when this work was initiated. Since then observations of such a process have been reported.[5]



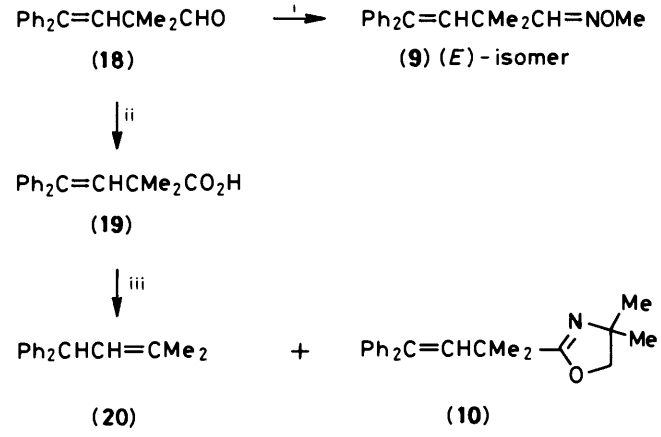
Synthesis of the Imino Compounds (**8**)—(**11**).—Treatment of the β,γ-unsaturated aldehyde (**14**)[6] with phenylmagnesium bromide followed by chromic acid oxidation of the resulting phenylmethanol (**15**) gave the β,γ-unsaturated ketone (**16**) (Scheme 2). Reaction of (**16**) with *O*-methylhydroxylamine yielded the (*E*)-compound (**8**) as the sole product, assignment of the configuration about the carbon–nitrogen double bond being based on ^{1}H n.m.r. spectral data (see later).

Reaction of the β,γ-unsaturated aldehyde (**18**)[7] with *O*-methylhydroxylamine provided the corresponding oxime ether (Scheme 3), assumed to be the less sterically crowded (*E*)-isomer (**9**).

Oxidation of the aldehyde (**18**) yielded the carboxylic acid (**19**), which upon treatment (Scheme 3) with 2-amino-2-methylpropanol gave the 4,5-dihydro-oxazole (**10**). The hydrocarbon (**20**) was obtained as a minor decarboxylation product. In the thermal decarboxylation of (**19**), either a concerted mechanism involving a six-centred cyclic transition state (**13a**) or an acid-catalysed process (**13b**) may operate leading to the non-conjugated product (**20**). A radical mechanism involving the allyl radical (**21**) may be excluded

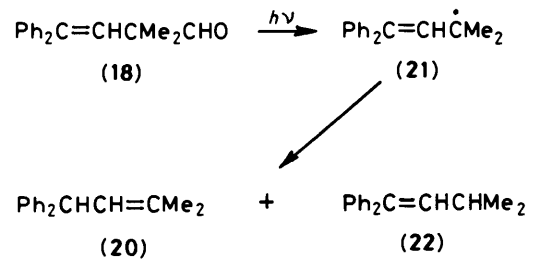


Scheme 2. *Reagents:* i, PhMgBr; ii, $Na_2Cr_2O_7$–H_2SO_4; iii, NH_2OMe; iv, *hν*



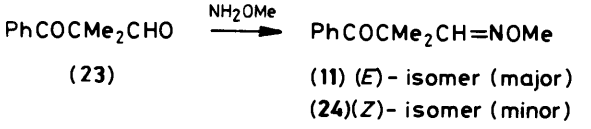
Scheme 3. *Reagents:* i, NH_2OMe; ii, CrO_3; iii, $HOCH_2CMe_2NH_2$

since in the photodecarbonylation of the aldehyde (**18**) (Scheme 4) disproportionation of (**21**) and formyl radicals leads to the conjugated hydrocarbon (**22**) as the major product, with (**20**) as the minor product.[8]



Scheme 4.

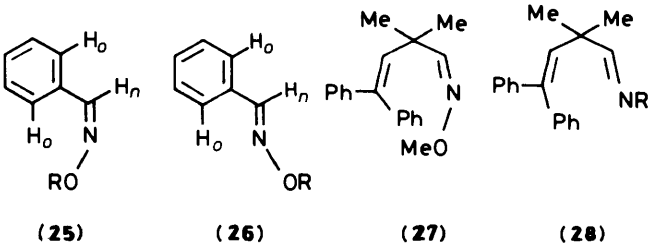
Reaction of the β-oxo aldehyde (**23**)[9] with *O*-methylhydroxylamine yielded the (*E*)-oxime ether (**11**), accompanied by the (*Z*)-isomer (**24**) as a minor product (Scheme 5). Assignment of configuration was based on the observation that the signal due to the oximino proton in the ^1H n.m.r. spectrum of the major product was merged with the aromatic signal at δ 7.43 and located at lower field than that due to the corresponding signal in the spectrum of the minor isomer at δ 6.99; the major isomer was, therefore, assigned the (*E*)-configuration (**11**). For aldoximes and their ethers it has been established[10] that the oximino proton (H_n) in the (*E*)-isomer, for example (**26**), is deshielded by the adjacent oxygen relative to that in the corresponding (*Z*)-isomer (**25**).

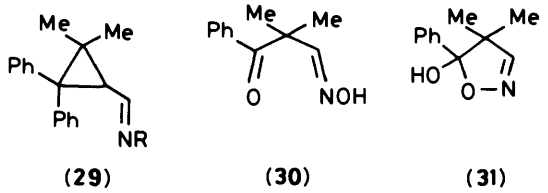


Scheme 5.

Photochemistry of β,γ-Unsaturated Imino Compounds (**8**), (**9**), *and* (**10**).—Photolysis of compound (**8**) in ethanol at wavelengths greater than 230 nm led to the formation of a single photoproduct (Scheme 2). Continued irradiation yielded a photostationary state with the starting material (**8**) and the photoproduct present in a 2:1 ratio, respectively. The photoproduct proved to be a photoisomer of (**8**), differing only in having the alternative configuration about the carbon–nitrogen double bond. The i.r. spectrum of the photoproduct confirmed the presence of both a carbon–nitrogen double bond (weak absorption at 1 635 cm^{-1}) and a carbon–carbon double bond (weak absorption at 1 590 cm^{-1}). Additionally the n.m.r. spectrum confirmed the presence of Me_2C=CH, OMe, gem-dimethyl, and phenyl groups, consistent with the assignment of structure (**17**) to the photoproduct.

That the photoproduct had the (*Z*)-structure (**17**) was supported by a comparison of the n.m.r. spectra of the two geometrical isomers. It has been established[10,11] that for oximes and oxime ethers such as (**25**) and (**26**) orientation of the oxygen *cis* to the phenyl group, as in (**25**), results in a deshielding of the two *ortho* protons (H_o) relative to that observed when the oxygen is *trans* to the phenyl group, as in (**26**). The photoproduct had a single signal at δ 7.23 (5 H, s, ArH) whereas the other isomer had two, at δ 6.98 (2 H, m, ArH) and 7.22 (3 H, m, ArH). The photoproduct, having the more deshielded aromatic protons, may therefore be assigned the (*Z*)-structure (**17**) whilst the isomeric oxime ether derived by reaction of ketone (**16**) with *O*-methylhydroxylamine may be assigned the (*E*)-structure (**8**).





Irradiation of an acetone solution of the (*E*)-isomer (**8**) at wavelengths > 300 nm resulted in the establishment of the same photoequilibrium between (**8**) and (**17**). Under otherwise identical conditions, but in ethanol as the solvent, only trace amounts of (**17**) were formed, absorption by (**8**) above 300 nm being extremely weak. Photoequilibration in acetone therefore

involved the intermediacy of triplet excited (**8**) formed by acetone sensitisation. The direct irradiation equilibration in ethanol at shorter wavelengths is consistent with the photoisomerisation proceeding from either the singlet excited state or the triplet excited state following intersystem crossing from the singlet.

Padwa and Albrecht have shown[12] that excitation of the carbon–nitrogen double bond of acetophenone oxime *O*-methyl ether leads to (*E*),(*Z*)-photoisomerisation. For compound (**8**) it is to be expected that initial excitation also involves the PhC=N chromophore and it is perhaps not surprising that geometrical isomerisation of this group is observed. No evidence was detected for the operation of any competing process, suggesting that *cis-trans* isomerisation is the process of lowest energy demand for the oxime ether (**8**).

The oxime ether (**9**) was chosen for investigation since initial excitation would involve the diphenylethylene chromophore. Geometrical isomerisation of the carbon–carbon double bond would not lead to new product formation and, if operational, alternative photoprocesses might be observable. However, direct or sensitised irradiation of the oxime ether (**9**) did not yield any isolable photoproduct, unchanged (**9**) being recovered. N.m.r. analysis of the crude photolysate revealed that some conversion had occurred to yield apparently two photoproducts in trace amounts. These could not be detected by t.l.c. and all efforts to isolate them by preparative chromatography were unsuccessful. One of the products may possibly have been the more hindered geometrical isomer (**27**) since additional singlet resonances were present which could be attributed to OMe, CH=CPh$_2$, and CH=N.

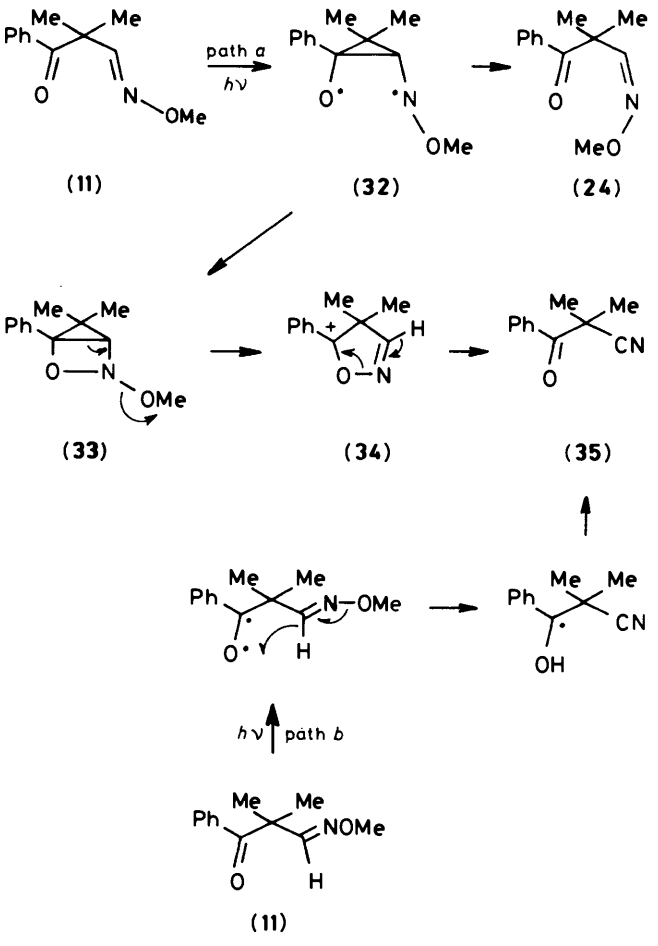
Compound (**10**), related to (**9**) in that excitation should again be initially in the diphenylethylene chromophore, was also irradiated. Inclusion of the carbon–nitrogen double bond in a ring precludes *cis-trans* isomerisation. However, (**10**) proved to be photochemically inert on both direct and sensitised irradiation. No evidence for photoproduct formation was obtained.

The absence of efficient product formation from either (**9**) or (**10**) may simply be due to carbon–carbon double bond isomerisation being the process of lowest energy demand, such isomerisation not leading to new product formation. Apparently, 2,4-bridging between the carbon–carbon and carbon–nitrogen double bonds leading to rearrangement (see Scheme 1) is particularly inefficient for (**9**) and (**10**). This is in marked contrast to observations reported[5c] for the closely related β,γ-unsaturated imines (**28**) which undergo rearrangement to structure (**29**).

Attempts to synthesize compound (**12**) by reaction of the oxo oxime ether (**11**) with, methylenetriphenylphosphorane or with methylmagnesium iodide followed by dehydration were unsuccessful. It had been hoped that an alternative substitution pattern on the excited chromophore might uncover new photochemical processes.

Photochemistry of the β-*Oxo Imino Compound* (**11**).—Direct irradiation of the (*E*)-compound (**11**) in ethanol yielded two photoproducts (Scheme 6). One of these was the isomeric (*Z*)-oxime ether (**24**). The i.r. spectrum of the other photoproduct showed the presence of cyano and carbonyl groups whilst the n.m.r. spectrum revealed the presence of two identical methyls and a phenyl group. The data were consistent with this product being 2-benzoyl-2-methylpropiononitrile (**35**), formed by the photoelimination of methanol. An attempt to confirm this identity by independent synthesis involving conversion of the β-oxo aldehyde (**23**) into the oxime (**30**) followed by dehydration to (**35**) was unsuccessful. Reaction of (**23**) with hydroxylamine yielded the 4,5-dihydroisoxazole (**31**), similar to the cyclisations previously reported[13] for reaction of benzoylacetaldehyde and benzoylacetone with hydroxylamine. Treatment of (**31**) under acidic conditions led to complex product mixtures from which the nitrile (**35**) was absent.

Initial excitation of (**11**) might be expected to be localised in the benzoyl group. Formation of compounds (**24**) and (**35**) by simple intramolecular energy transfer, followed by geometrical isomerisation and elimination of methanol from the resulting methoxyimino excited state, seems unlikely from energy considerations. A process involving bonding between the two groups is suggested as one possibility (Scheme 6, path *a*).



Scheme 6.

Bridging of excited (**11**) to form (**32**) could account for the formation of both observed products. Thus free rotation around the carbon–nitrogen single bond in (**32**), followed by reopening of the three-membered ring, would lead to the geometrical isomer (**24**). In addition, closure of (**32**) to the strained heterocycle (**33**) followed by elimination of methoxide ion and ring-opening of (**34**) would lead to the nitrile (**35**). Alternatively, the nitrile (**35**) might be formed (Scheme 6, path *b*) by N–O bond fragmentation, initiated by intramolecular hydrogen abstraction by the excited benzoyl group of (**11**) and followed by disproportionation. A related intermolecular process has been reported[14] for the reaction of benzophenone triplet with *N*-benzylidene-t-butylamine in benzene leading to formation of benzonitrile and t-butylbenzene.

Experimental

General.—Flash chromatography was carried out using the method of Still *et al.*,[15] using Koch-Light silica gel (Art. 7729),

finer than 230 mesh. T.l.c. was carried out on silica gel using Kodak-Eastman chromatogram sheets incorporating fluorescent indicator 6060. Light petroleum for chromatography refers to the fraction b.p. 40—60 °C. I.r. spectra were recorded on a Perkin-Elmer 197 double beam instrument. Spectra reported for oils are for neat liquid samples examined as capillary films between sodium chloride plates. Spectra reported for solids are for Nujol mulls. U.v. spectra were recorded on a Cary 118X (800—200 nm) spectrometer and are reported for solutions in ethanol. N.m.r. spectra were recorded on either Perkin-Elmer–Hitachi R20A or R32A spectrometers operating at 60 or 90 MHz respectively. They are reported for carbon tetrachloride or deuteriochloroform solutions with $SiMe_4$ as internal reference.

Photochemical reactions were performed with photolysis solutions placed in a cylindrical vessel surrounding a water-cooled quartz immersion well carrying a Hanovia 200-W medium-pressure mercury vapour lamp fitted with a Vycor or Pyrex filter sleeve. A stream of nitrogen was bubbled through the photolysis solutions prior to and during irradiation.

2,2,4-*Trimethylpent*-3-*enal* (**14**).—The β,γ-unsaturated aldehyde (**14**) was prepared by acid-catalysed dehydration of a mixture of *cis*- and *trans*-2,2,4,4-tetramethylcyclobutane-1,3-diol as previously described by Hasek and co-workers.[6]

Preparation of 2,2,4-*Trimethyl*-1-*phenylpent*-3-*en*-1-*ol* (**15**).—Phenylmagnesium bromide was prepared by carefully adding bromobenzene (15.7 g) in dry ether (50 ml) to magnesium turnings (2.5 g) in dry ether (40 ml). The reaction mixture was heated under reflux for 1 h and then cooled to 5 °C in an ice-bath. A solution of (**14**) (10.0 g) in dry ether (50 ml) was slowly introduced whilst maintaining the temperature below 15 °C. The reaction mixture was left overnight and then hydrolysed by careful addition of saturated aqueous ammonium chloride (150 ml); it was then extracted with ether and the extract dried ($MgSO_4$) and concentrated. Distillation of the resulting oil yielded the title compound (**15**) (13.1 g, 81%), b.p. 94—95 °C/0.8 mmHg; $\nu_{max.}$ 3 650—3 200br (OH), 1 600 (C=C), and 1 045 and 1 030 cm^{-1} (C–O); δ 1.01 (s, 6 H, CMe_2), 1.65 (d, 3 H, *J* 1.5 Hz, MeC=C), 1.71 (d, 3 H, *J* 1.5 Hz, MeC=C), 2.70 (s, 1 H, OH, removed by shaking with D_2O), 4.45 (s, 1 H, CHO), 5.09 (m, 1 H, HC=C), and 7.20 (s, 5 H, phenyl) (Found: C, 82.1; H, 9.6. $C_{14}H_{20}O$ requires C, 82.35; H, 9.8%).

Preparation of 2,2,4-*Trimethyl*-1-*phenylpent*-3-*en*-1-*one* (**16**).—To a stirred solution of the alcohol (**15**) (10.17 g) in ether (10 ml) was added, over a 3 h period and below 15 °C, a chromic acid solution prepared from sodium dichromate dihydrate (5.05 g) and concentrated sulphuric acid (3.75 ml) which had been diluted to 25 ml. The mixture was stirred for 4 h after which the ether layer was separated and the aqueous phase extracted with ether (3 × 30 ml). The combined extracts were washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated. Distillation of the resulting oil yielded the title compound (**16**) (7.47 g, 74%), b.p. 93—95 °C/0.5 mmHg; $\nu_{max.}$ 1 650 (C=O) and 1 600 (C=C) cm^{-1}; δ 1.32 (d, *J* 1.5 Hz, 3 H, MeC=C), 1.34 (s, 6 H, CMe_2), 1.68 (d, *J* 1.5 Hz, 3 H, MeC=C), 5.55 (m, 1 H, HC=C), 7.40 (m, 3 H, ArH), and 8.0 (m, 2 H, aromatic) (Found: C, 82.9; H, 8.9. $C_{14}H_{18}O$ requires C, 83.1; H, 9.0%).

Preparation of (E)-N-*Methoxy* 2,2,4-*trimethyl*-1-*phenylpent*-3-*en*-1-*imine* (**8**).—To a solution of *O*-methylhydroxylamine hydrochloride[16] (3.86 g) in pyridine (10 ml) was added a solution of ketone (**16**) (4.93 g) in pyridine (10 ml). The reaction mixture was heated under reflux for 8 h, cooled, poured into water, and extracted with ether. The extract was washed thoroughly with water, dried ($MgSO_4$), and concentrated. Distillation of the resulting oil gave the *title compound* (**8**) (4.22 g, 73%), b.p. 95—97 °C/0.5 mmHg, $\nu_{max.}$ 1 660 (C=N), 1 598 (C=C), and 1 070 cm^{-1} (C–O); δ 1.25 (s, 6 H, CMe_2), 1.70 (d, *J* 1.5 Hz, 3 H, MeC=C), 1.77 (d, *J* 1.5 Hz, 3 H, MeC=C), 3.71 (s, 3 H, OMe), 5.03 (m, 1 H, HC=C), 6.98 (m, 2 H, ArH), and 7.22 (m, 3 H, ArH); $\lambda_{max.}$ 262 nm (ε 650) (Found: C, 78.2; H, 9.1; N, 5.8. $C_{15}H_{21}NO$ requires C, 77.9; H, 9.1; N, 6.05%).

Preparation of 2,2-*Dimethyl*-4,4-*diphenylbut*-3-*enal* (**18**).—The β,γ-unsaturated aldehyde (**18**) was prepared as previously described.[7]

Preparation of N-*Methoxy*-2,2-*dimethyl*-4,4-*diphenylbut*-3-*en*-1-*imine* (**9**).—To a solution of *O*-methylhydroxylamine hydrochloride (2.17 g) in pyridine (5 ml) was added a solution of the aldehyde (**18**) (4.34 g) in pyridine (5 ml). The mixture was heated for 12 h under reflux after which it was treated as described for (**8**). Distillation yielded the *title compound* (**9**) (3.33 g, 69%), b.p. 140—143 °C/0.5 mmHg; $\nu_{max.}$ 1 620 (C=N), 1 600 C=C), and 1 060 cm^{-1} (C–O); δ 1.17 (s, 6 H, CMe_2), 3.49 (s, 3 H, OMe), 5.94 (s, 1 H, HC=C), 6.87 (s, 1 H, HC=N), and 7.18 (m, 10 H, ArH); $\lambda_{max.}$ 248 nm (ε 13 500) (Found: C, 81.9; H, 7.7; N, 4.8. $C_{19}H_{21}NO$ requires C, 81.7; H, 7.6; N, 5.0%).

Preparation of 2,2-*Dimethyl*-4,4-*diphenylbut*-3-*enoic Acid* (**19**).—A solution of chromium trioxide (2.5 g) in water (15 ml) containing concentrated sulphuric acid (2 ml) was added dropwise with stirring to a solution of the aldehyde (**18**) (6.0 g) in acetone (15 ml; previously distilled over potassium permanganate) at 0—15 °C. The mixture was stirred for a further 30 min and then diluted with water and extracted with ether (3 × 50 ml). The ether extract was washed with 10% aqueous sodium hydroxide (2 × 50 ml) and then with water, until the washings were neutral to litmus. The organic phase was dried ($MgSO_4$) and concentrated to give unchanged (**18**) (4.2 g).

The aqueous alkaline layer was acidified with concentrated hydrochloric acid and then extracted with ether (3 × 50 ml). The extract was washed thoroughly with water, dried ($MgSO_4$), and concentrated to give a yellow liquid which was recrystallised from ethanol to afford white crystals of the *title compound* (**19**) (1.63 g, 85% based on consumed starting material), m.p. 95—97 °C; $\nu_{max.}$ 3 030—2 725br (OH), and 1 702 cm^{-1} (C=O); δ 1.28 (s, 6 H, CMe_2), 6.10 (s, 1 H, HC=C), 7.19 (m, 10 H, ArH) and 14.5 (br, 1 H, CO_2H) (Found: C, 81.3; H, 6.9. $C_{18}H_{18}O_2$ requires C. 81.2; H, 6.8%).

Preparation of 2-(1,1-*Dimethyl*-3,3-*diphenylprop*-2-*enyl*)-4,4-*dimethyl*-4,5-*dihydro-oxazole* (**10**).—Compound (**10**) was prepared by a standard method[17] involving heating a mixture of unsaturated acid (**19**) (1.84 g) and 2-amino-2-methylpropanol (7.3 g) at 165—170 °C for 30 h. The mixture was cooled, dissolved in ether (100 ml) and the solution washed with 10% aqueous potassium hydroxide (2 × 50 ml) and water and dried ($MgSO_4$). Concentration gave an oil (1.75 g) which was subjected to flash chromatography. Elution was initially with light petroleum, the polarity of the mobile phase being gradually increased by adding ethyl acetate up to 20%. The first component eluted was 3-methyl-1,1-diphenylbut-2-ene (**20**) (0.15 g, 10%) identified by comparison of its spectral properties (i.r., n.m.r.) with those previously reported for compound (**20**).[8] The second component eluted was purified by distillation to give the *title compound* (**10**) (0.75 g, 34%), b.p. 140—142 °C/0.5 mmHg; $\nu_{max.}$ 1 660 (C=N), 1 600 (C=C), and 1 110 cm^{-1} (C–O); δ 1.01 (s, 6 H, CMe_2), 1.25 (s, 6 H, CMe_2), 3.49 (s, 2 H, OCH_2), 6.02 (s, 1 H, CH=C), and 7.18 (m, 10 H, ArH); $\lambda_{max.}$ 246 nm (ε 13 450) (Found: C, 82.9; H, 8.2; N, 4.0. $C_{22}H_{25}NO$ requires C, 82.7; H, 7.9; N, 4.4%).

Preparation of 2-*Benzoyl*-2-*methylpropanal* (**23**).—The β-oxo aldehyde (**23**) was prepared by reaction of benzoyl chloride with 1-morpholino-2-methylpropene,[18] this enamine being prepared as previously described in the literature.[19]

Preparation of 2-*Benzoyl*-(E)-N-*methoxy*-2-*methylpropan*-1-*imine* (**11**).—A solution of 2-benzoyl-2-methylpropanal (**23**) (7.0 g) in ethanol (30 ml) was added to a solution of sodium acetate trihydrate (10.0 g) in water (15 ml) after which *O*-methylhydroxylamine hydrochloride (7.0 g) in ethanol (30 ml) was added dropwise at 25 °C with stirring. After 2 h most of the ethanol was removed under reduced pressure and the residue was extracted with ether. The extract was washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated to give an oil (7.6 g) which was subjected to flash chromatography. Elution with light petroleum yielded two components.

The first component to be collected was further purified by distillation to give the *title compound* (**11**) (6.1 g, 74%), b.p. 92—94 °C/0.5 mmHg; $\nu_{max.}$ 1 680 (C=O), 1 600 (C=N), and 1 060 cm^{-1} (C–O); δ 1.45 (s, 6 H, CMe_2), 3.83 (s, 3 H, OMe), 7.43 (m, 4 H, CH=N and ArH), and 7.88 (m, 2 H, ArH); $\lambda_{max.}$ 317 nm (ε 134) (Found: C, 70.6; H, 7.7; N, 7.0. $C_{12}H_{15}NO_2$ requires C, 70.2; H, 7.4; N, 6.8%).

The second component to be collected was further purified by distillation to give 2-*benzoyl*-(Z)-N-*methoxy*-2-*methylpropan*-1-*imine* (**24**) (0.52 g, 6%), b.p. 89—91 °C/0.5 mmHg; $\nu_{max.}$ 1 690 (C=O), 1 580 (C=N), and 1 050 cm^{-1} (C–O); δ 1.40 (s, 6 H, CMe_2), 3.38 (s, 3 H, OMe), 6.99 (s, 1 H, CH=N), 7.40 (m, 3 H, ArH), and 7.90 (m, 2 H, ArH); $\lambda_{max.}$ 239 nm (ε 9 500) (Found: C, 70.4; H, 7.5; N, 7.0%).

Photolysis of (E)-N-*Methoxy*-2,2,4-*trimethyl*-1-*phenylpent*-3-*en*-1-*imine* (**8**).—(*a*) *In ethanol at* λ > 230 *nm.* Compound (**8**) (1.02 g) in ethanol (480 ml) was irradiated through Vycor, the progress of the reaction being monitored by t.l.c., g.l.c. (PEGA, 0.25 in × 10 ft, 180 °C) and n.m.r. A single photoproduct formed, the geometrical isomer (**17**). After 9.5 h, a photostationary state had been established, 2:1 in favour of the (*E*)-isomer (**8**).

(*b*) *In ethanol or ether at* λ > 300 *nm.* Compound (**8**) (1.94 g) in ethanol or ether (450 ml) was irradiated through Pyrex, progress being monitored as in (*a*). After 9.5 h, only a trace amount of (**17**) could be detected.

(*c*) *In acetone at* λ > 300 *nm.* Compound (**8**) (3.0 g) in acetone (450 ml) was irradiated through Pyrex, progress being monitored as in (*a*). Again a 2:1 photostationary state was established. After 10 h, removal of the solvent gave a yellow liquid which was subjected to flash chromatography, elution being with light petroleum. The first component to be eluted was the (*E*)-oxime ether (**8**) (1.87 g, 62%) identified by spectral comparison with an authentic sample. The second component to be eluted was further purified by distillation to give (Z)-N-*methoxy*-2,2,4-*trimethyl*-1-*phenylpent*-3-*en*-1-*imine* (**17**) (0.88 g, 29%), b.p. 89 °C/0.5 mmHg; $\nu_{max.}$ 1 635 (C=N), 1 590 (C=C), and 1 059 cm^{-1} (C–O); δ 1.26 (s, 6 H, CMe_2), 1.55 (d, *J* 1.5 Hz, 3 H, MeC=C), 1.64 (d, *J* 1.5 Hz, 3 H, MeC=C), 3.77 (s, 3 H, OMe), 5.24 (m, 1 H, CH=C), and 7.23 (s, 5 H, ArH); $\lambda_{max.}$ 230 (ε 6 700) (Found: C, 79.3, 80.0; H, 10.0, 10.1; N, 4.5, 5.3. $C_{15}H_{21}NO$ requires C, 77.9; H, 9.1; N, 6.05%).

Irradiation of N-*Methoxy*-2,2-*dimethyl*-4,4-*diphenylbut*-3-*en*-1-*imine* (**9**).—Samples of compound (**9**) were irradiated through Vycor under the following conditions: (*a*) 200 mg in ethanol (480 ml) for 24 h, (*b*) 200 mg in t-butyl alcohol (480 ml) for 24 h, (*c*) 310 mg in t-butyl alcohol (480 ml) containing acetophenone (680 mg) for 15 h, (*d*) 170 mg in ethanol (480 ml) containing 4-methoxyacetophenone (120 mg) for 15 h, (*e*) 300 mg in acetone (480 ml) for 15 h.

In each case n.m.r. analysis revealed the presence of trace amounts of two photoproducts as indicated by the appearance of two additional singlets at δ 3.79 and 3.95 (OMe region), 2 additional singlets at δ 6.08 and 6.20 ($CH=CPh_2$ region) and 1 additional singlet at δ 6.78 (CH=N region). All efforts to detect the photoproducts by t.l.c. or to isolate them by preparative chromatography were unsuccessful, only (**9**) being recovered in high yield.

Irradiation of 2-(1,1-*Dimethyl*-3,3-*diphenylprop*-2-*enyl*)-4,4-*dimethyl*-4,5-*dihydro*-*oxazole* (**10**).—Irradiation of the dihydrooxazole (**10**) (500 mg) in hexane or acetone (480 ml) through Vycor or Pyrex for 24 h, with t.l.c. and n.m.r. monitoring, revealed only the presence of unchanged (**10**) in the photolysed material. No evidence of any reaction was found.

Photolysis of 2-*Benzoyl*-(E)-N-*methoxy*-2-*methylpropan*-1-*imine* (**11**).—A solution of the (*E*)-oxime ether (**11**) (2.0 g) in ethanol (480 ml) was irradiated through Vycor for 3 h. T.l.c. and g.l.c. (APL, 0.5 in × 10 ft, 175 °C) showed two photoproducts. The solvent was removed and the photolysis mixture subjected to flash chromatography, elution being with light petroleum. The first component collected (0.42 g, 21%) was identified as starting material (**11**) by spectral and chromatographic comparison. The second component collected was 2-*benzoyl*-2-*methylpropiononitrile* (**35**) (0.43 g, 27%) which was further purified by preparative g.c. using a 5 m APL column at 175 °C; $\nu_{max.}$ 2 245 (cyano) and 1 690 cm^{-1} (C=O); δ 1.67 (s, 6 H, CMe_2), 7.53 (m, 3 H, ArH) and 8.19 (m, 2 H, ArH); *m/z* 173 (*M*, 1.2%), 105 (PhCO, 100%), and 77 (82%) (Found: C, 75.1; H, 6.6; N, 7.7. $C_{11}H_{11}NO$ requires C, 76.3; H, 6.3; N, 8.1%).

The third component collected was 2-benzoyl-(*Z*)-*N*-methoxy -2-methylpropan-1-imine (**24**) (0.37 g, 18%), identified by spectral and chromatographic comparison with an authentic sample.

Reaction of 2-*Benzoyl*-2-*methylpropanal* (**23**) *with Hydroxylamine.*—Hydroxylamine hydrochloride (2.7 g) in pyridine (10 ml) was added dropwise to a solution of the oxo aldehyde (**23**) (5.0 g) in pyridine (10 ml). After 2 h the mixture was poured into water (50 ml) and the product extracted with ether. The extract was washed thoroughly with water, dried ($MgSO_4$), and evaporated to give an oil which was subjected to flash chromatography. Elution was initially with light petroleum, the polarity of the mobile phase being gradually increased by the addition of ethyl acetate up to 10%. The first eluted band was a complex mixture of unidentified compounds (0.68 g). The second band to be eluted was recrystallised from carbon tetrachloride to give 4,5-*dihydro*-5-*hydroxy*-4,4-*dimethyl*-5-*phenylisoxazole* (**31**) (1.12 g, 21%), m.p. 70—72 °C; $\nu_{max.}$ 3 400—3 100br (OH), 1 610 (C=N), and 1 097 cm^{-1} (C–O); δ 0.58 (s, 3 H, Me), 1.29 (s, 3 H, Me), 3.46 (s, 1 H, OH, removed on shaking with D_2O), 6.93 (s, 1 H, CH=N), and 7.35 (m, 5 H, ArH); *m/z* 191 (*M*, 0.3%), 105 (PhCO, 100%), and 77 (53%) (Found: C, 69.2; H, 6.8; N, 7.4. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.8; N, 7.3%).

Acknowledgements

We are grateful to Dr. M. Barlow for assistance during the course of this work. Q. A-M. thanks the government of the Republic of Iraq for financial assistance.

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Received 16*th January* 1986; *Paper* 6/123.