

Photochemistry of the Carbon–Nitrogen Double Bond. Part 1. Carbon–Nitrogen vs. Carbon–Carbon Double Bond Isomerisation in the Photochemistry of α,β -Unsaturated Oxime Ethers: The Benzylideneacetone Oxime *O*-Methyl Ether System

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The syntheses of the four benzylideneacetone oxime *O*-methyl ether isomers (2)–(5) are described. Direct or sensitised irradiation of the *E,E*-isomer (2) or *Z,E*-isomer (3) leads to equilibration of all four isomers by a combination of rapid carbon–nitrogen double bond isomerisation and slower carbon–carbon double bond isomerisation. A previous investigation of the photochemistry of the *E,E*-isomer (2) had reported only carbon–carbon double bond isomerisation.

The photochemistry of systems containing carbon–oxygen and carbon–carbon double bonds has been much studied and is well understood. There has been less sustained interest in systems containing a carbon–nitrogen double bond though a wide variety of photoprocesses have been reported and classified.¹

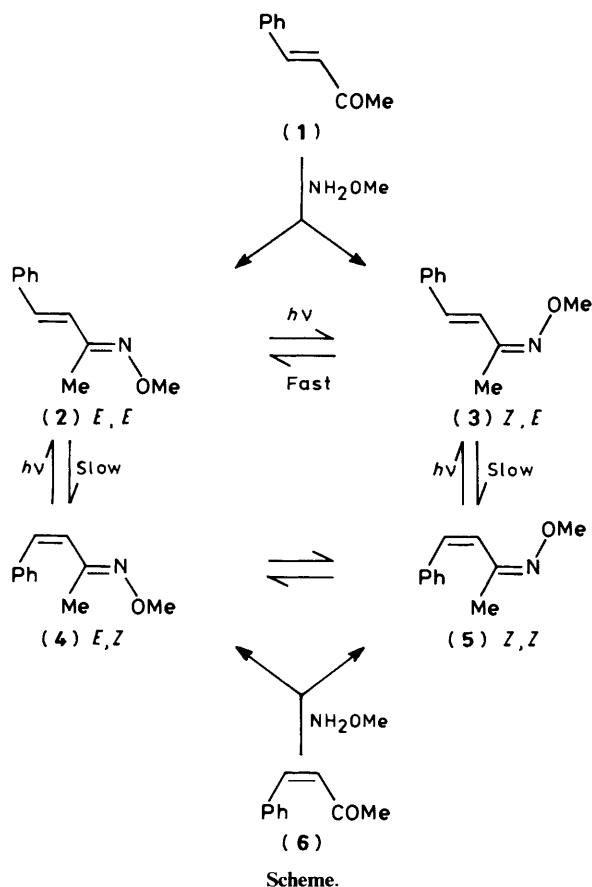
A report² that direct irradiation of a conjugated oxime ether, (*E*)-[(*E*)-benzylideneacetone] oxime *O*-methylether (2), resulted solely in *Z-E* isomerisation about the carbon–carbon double bond seems surprising when it is considered that oxime ethers undergo ready *Z-E* photoisomerisation about the carbon–nitrogen double bond.³ In compounds of this type four distinct

isomers, (2)–(5), are possible and irradiation of the *E,E*-isomer (2) might be expected to result in *Z-E* isomerisation about the carbon–nitrogen double bond as well as *Z-E* isomerisation about the carbon–carbon double bond. In view of this expectation we have reinvestigated the photochemistry of the *E,E*-oxime ether (2), in addition to that of the *Z,E*-isomer (3).

Synthesis and Characterisation of the Oxime Ether Isomers (2)–(5).—Reaction of *E*-benzylideneacetone (1) with *O*-methylhydroxylamine yielded the isomeric oxime ethers (2) (major product) and (3) (minor product), identified by comparison with published data for these previously characterised compounds.^{4,5} Similar reaction of *Z*-benzylideneacetone (6) with *O*-methylhydroxylamine yielded a mixture of oxime ethers (4) and (5) which were separated by preparative gas chromatography. The isomers with longer and shorter g.c. retention times have been tentatively assigned the structures (4) and (5), respectively, based on u.v. and t.l.c. observations.

It has been reported that the *Z*-oxime derivatives of a range of α,β -unsaturated ketones and aldehydes (7),⁶ and also the *Z*-isomer of 3-ethoxyiminobutan-2-one (8),⁷ absorb maximally at longer wavelength and with less intensity than the corresponding *E*-isomers. Compound (4) exhibits absorption maxima at 264 and 231 nm (ϵ 13 750 and 8 350 respectively) whereas compound (5) absorbs maximally at 259 and 231 nm (ϵ 12 200 and 6 700 respectively). The extinction coefficients are smaller for the isomer assigned the *Z,Z*-structure (5). This trend is similar to that observed for the *E,E*- and *Z,E*-isomers (2) and (3).

Unterhalt has reported⁶ that *E*-oximes derived from α,β -unsaturated ketones and aldehydes (7) have higher R_f values on t.l.c. than the corresponding *Z*-oximes. The isomer assigned the *E*-configuration around the carbon–nitrogen double bond, *i.e.* structure (4), has a higher R_f value on t.l.c. than the isomer assigned the *Z*-configuration, *i.e.* structure (5). This is identical to that observed for isomers (2) and (3), providing support for the assignment of structures (4) and (5).



Photochemistry of the *E,E*- and *Z,E*-Isomers (2) and (3).—The *E,E*-isomer (2) was irradiated directly in ethanol ($\lambda > 300$ nm). Only the *Z,E*-isomer (3) could be detected as the sole photo-

product during the early stages of the reaction. However, prolonged irradiation resulted in the additional formation of the *Z,Z*-isomer (5) as well as a trace of the *E,Z*-isomer (4). The same photostationary state (see the Experimental section) is eventually reached irrespective of whether (2) or (3) is initially irradiated. No other photoproducts were observed at any stage.

These observations are summarised in the Scheme. They can be explained in terms of an initial fast process involving *Z-E* isomerisation around the carbon–nitrogen double bond, which results in the equilibration of the *E,E*- and *Z,E*-isomers (2) and (3), followed by a slower process involving *Z-E* isomerisation around the carbon–carbon double bonds of (2) and (3), resulting in the formation of compounds (4) and (5). Presumably the *E,Z*- and *Z,Z*-isomers (4) and (5) also undergo rapid photoequilibration by carbon–nitrogen double bond isomerisation. Unfortunately, only small amounts of very pure (4) and (5) could be collected and for this reason the photochemistry of these isomers was not investigated.

The isomerisations, resulting from direct irradiation of either isomers (2) or (3), could have occurred from either a singlet excited state or, following intersystem crossing, a triplet excited state of the oxime ether. The triplet excited states, when generated directly, also lead to equilibration. Thus, triplet sensitisation of either (2) or (3) by 4-methoxyacetophenone initially produced carbon–nitrogen double bond isomerisation in each case, prolonged sensitisation leading also to slower carbon–carbon double bond isomerisation. Carbon–nitrogen double bond isomerisation, therefore, is a more facile process than carbon–carbon double bond isomerisation for this conjugated system, though both are observed to occur.

It had previously been reported² that, on direct irradiation of the *E,E*-isomer (2) only carbon–carbon double bond isomerisation occurs. The n.m.r. spectrum reported² for compound (2), is very similar to that recorded in our work, confirming the identity of the starting oxime ethers. That the product, isolated by preparative gas chromatography, had a *Z*-1,2-disubstituted carbon–carbon double bond is also beyond question, the authors reporting² a coupling constant of 12 Hz for the vinyl protons. However, their assignment of the *E*-configuration about the carbon–nitrogen double bond was not justified in any way. Comparison of data suggests that the product which they isolated was the one to which we have tentatively assigned structure (5) and which is the major product formed on prolonged direct irradiation of the *E,E*-isomer (2). Whilst compound (2) and the initial rapidly-formed product (3) can be readily separated analytically by h.p.l.c. and preparatively by silica gel column chromatography, we have been unable to separate them on a variety of g.c. columns (SE30, PEGA, APL, DNP, TXP, and FS-1265). This may explain the discrepancy, product (3) not having been detected previously during g.c. analysis² and the trace product, to which we have tentatively assigned structure (4), not having been reported.

Experimental

Column chromatography used conventional columns packed with 80–200 mesh chromatographic grade silica gel. Flash chromatography was carried out using the method of Still *et al.*,⁸ using Koch-Light silica gel 60 (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 had b.p. 40–60 °C. Gas chromatography (g.c.) was carried out on a Pye-Unicam GCD chromatograph. H.p.l.c. analysis utilised an Applied Chromatography System reciprocating pump (model 750.03), with detection by a Cecil variable wavelength detector (CE212). Columns used were (a) 20 × 0.46 cm Aminospherisorb (5 μ) with elution by 10% dichloromethane in light petroleum,

and (b) 20 × 0.46 cm Partisil (5 μ) with elution by 25% dichloromethane in light petroleum.

I.r. spectra were recorded on a Perkin-Elmer 197 double beam instrument. Spectra reported are for neat liquid samples examined as capillary films between sodium chloride plates. 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 solutions with Me₄Si as the internal reference.

Photochemical reactions were carried out in a cylindrical vessel surrounding a water-cooled quartz immersion well carrying a Hanovia 200 W medium pressure mercury vapour lamp fitted with a Pyrex filter sleeve ($\lambda > 300$ nm). A stream of nitrogen was bubbled through the photolysis solution prior to and during irradiation.

Preparation of (E)-[(E)-Benzylideneacetone] Oxime O-Methyl Ether (2) and (Z)-[(E)-Benzylideneacetone] Oxime O-Methyl Ether (3).—(*E*)-Benzylideneacetone (1)⁹ (7.0 g) in ethanol (25 ml) was added to a solution of sodium acetate trihydrate (6.8 g) in water (10 ml). Then *O*-methylhydroxylamine hydrochloride¹⁰ (5.0 g) in ethanol (25 ml) was added dropwise with stirring. After 30 min, the mixture was poured into water (100 ml) and extracted thoroughly with diethyl ether. The extract was washed successively with 5% aqueous sodium hydrogen carbonate and water, and dried (MgSO₄). Removal of the ether gave a yellow liquid (7.3 g) which was applied to a flash chromatography column and eluted with light petroleum.

The first component to be eluted was distilled under vacuum (b.p. 110–112 °C/0.5 mmHg) to give colourless (*E*)-[(*E*)-benzylideneacetone] oxime *O*-methyl ether (2) (4.6 g): λ_{\max} 286 nm (ϵ 31 700); δ 1.99 (s, 3 H, CMe), 3.88 (s, 3 H, OMe), 6.74 (s, 2 H, vinylic), and 7.35 (m, 5 H, ArH) (Found: C, 75.1; H, 7.5; N, 7.7. C₁₁H₁₃NO requires C, 75.39; H, 7.47; N, 7.99%).

The second component to be eluted was also distilled under vacuum (b.p. 119–121 °C/0.5 mmHg) to give colourless (*Z*)-[(*E*)-benzylideneacetone] oxime *O*-methyl ether (3) (1.5 g): λ_{\max} 291 nm (ϵ 20 300); δ 2.01 (s, 3 H, CMe), 3.82 (s, 3 H, OMe), 6.74 (d, 1 H, *J* 16.5 Hz, vinylic H), and 7.35 (m, 6 H, ArH and vinylic H) (Found: C, 75.2; H, 7.2; N, 7.9%).

Preparation of (E)-[(Z)-Benzylideneacetone] Oxime O-Methyl Ether (4) and (Z)-[(Z)-Benzylideneacetone] Oxime O-Methyl Ether (5).—(*Z*)-Benzylideneacetone (6) was prepared¹¹ by irradiation of (*E*)-benzylideneacetone (1) (7.0 g) in methanol (450 ml) at wavelengths > 300 nm for 2 h. The solvent was removed and the mixture applied to a flash chromatography column and eluted with light petroleum. (*Z*)-Benzylideneacetone (6) (3.3 g) [δ 2.01 (s, 3 H, CMe), 6.5 (d, 1 H, *J* 12 Hz, vinylic H), 6.75 (d, 1 H, *J* 12 Hz, vinylic H), and 7.31 (m, 5 H, ArH)] eluted first, followed by (*E*)-benzylideneacetone (1) (3.2 g), and was used without further purification.

(*Z*)-Benzylideneacetone (6) (1.28 g) in ethanol (5 ml) was added dropwise with stirring to a solution of *O*-methylhydroxylamine hydrochloride¹⁰ (0.08 g) in pyridine (10 ml). After 1 h the mixture was extracted with ether, washed with water, and dried (MgSO₄). Removal of the ether gave a colourless liquid (1.33 g) which was shown (n.m.r. and g.c.) to be a mixture of the oxime ethers (4) and (5). Separation was effected by preparative g.c. using a 4m APL column at 190 °C.

The first component to be collected was (*Z*)-[(*Z*)-benzylideneacetone] oxime *O*-methyl ether (5) (0.11 g): λ_{\max} 259 (ϵ 12 200) and 234 nm (ϵ 6 700); δ 1.69 (s, 3 H, CMe), 3.80 (s, 3 H, OMe), 6.25 (d, *J* 12 Hz, 1 H, vinylic H), 6.61 (d, *J* 12 Hz, 1 H, vinylic H), and 7.21 (s, 5 H, ArH) (Found: C, 75.1; H, 7.5; N, 7.7%).

The second component to be collected was (*E*)-[(*Z*)-benzylideneacetone] oxime *O*-methyl ether (**4**) (0.15 g): λ_{\max} 264 (ϵ 13 750) and 231 nm (ϵ 8 353); δ 1.60 (s, 3 H, CMe), 3.86 (s, 3 H, OMe), 6.15 (d, *J* 12 Hz, 1 H, vinylic H), 6.70 (d, *J* 12 Hz, 1 H, vinylic H), and 7.22 (s, 5 H, ArH) (Found: C, 75.7; H, 7.2; N, 8.3%).

Direct Irradiation of (E)-[(E)-Benzylideneacetone] Oxime O-Methyl Ether (2).—The oxime ether (**2**) (1.03 g) in ethanol (450 ml) was irradiated whilst monitoring the progress of the reaction using t.l.c. and h.p.l.c. analysis. After 10 min a single photoproduct, the *Z,E*-isomer (**3**), had formed. Further irradiation resulted in the gradual appearance of the *Z,Z*-isomer (**5**) and a trace of the *E,Z*-isomer (**4**). At the end of 4 h a photostationary state had been established. H.p.l.c. analysis revealed the presence of (**2**), (**3**), (**4**), and (**5**) in the ratio 46:17:3:34 respectively.

Preparative layer chromatography separation of the mixture yielded the unchanged compound (**2**) (0.41 g), the *Z,Z*-isomer (**5**) (0.32 g), and the *Z,E*-isomer (**3**) (0.15 g) in order of elution.

Direct Irradiation of (Z)-[(E)-Benzylideneacetone] Oxime O-Methyl Ether (3).—Similar treatment of isomer (**3**) (1.10 g) showed the *E,E*-isomer (**2**) as the only detectable photoproduct after 10 min. Further irradiation led to the gradual appearance of compound (**5**) and a trace of the isomer (**4**). At the end of 4 h the same photostationary state had been established.

4-Methoxyacetophenone Sensitisation of the E,E-Isomer (2).—A solution of oxime ether (**2**) (1.0 g) in ethanol (10 ml) containing 4-methoxyacetophenone (4.3 g, sufficient to absorb greater than 95% of the incident radiation) was irradiated at 254 nm. After 8 h, h.p.l.c. analysis revealed the presence of the *Z,E*-isomer (**3**) as the major photoproduct along with a trace of the *Z,Z*-isomer (**5**). Column chromatography of the mixture on silica gel, eluting with 5% diethyl ether in light petroleum, yielded recovered (**2**) (0.61 g) and the *Z,E*-isomer (**3**) (0.32 g).

Repetition of this experiment, but with longer irradiation, led to the continued slow build-up of the *Z,Z*-isomer (**5**) and appearance of a trace of the *Z,E*-isomer (**4**). Preparative t.l.c. after 240 h irradiation yielded recovered (**2**) (0.48 g) along with two photoproducts, the *Z,E*-isomer (**3**) (0.12 g) and the *Z,Z*-isomer (**5**) (0.23 g).

4-Methoxyacetophenone Sensitisation of the Z,E-Isomer (3).—A solution of the oxime ether (**3**) (1.07 g) in ethanol (10 ml) containing 4-methoxyacetophenone (4.3 g) was irradiated at 254 nm. After 8 h, h.p.l.c. analysis revealed the presence of the *E,E*-isomer (**2**) as the major photoproduct along with a trace of the *Z,Z*-isomer (**5**). Column chromatography of the mixture yielded recovered (**3**) (0.42 g) and the *E,E*-isomer (**2**) (0.55 g).

Repetition with longer irradiation led to the continued slow build-up of the *Z,Z*-isomer (**5**) and the appearance of a trace of the *E,Z*-isomer (**4**). Preparative t.l.c. after 240 h irradiation yielded recovered (**3**) (0.17 g) along with two photoproducts, the *E,E*-isomer (**2**) (0.45 g) and the *Z,Z*-isomer (**5**) (0.19 g).

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 11th October 1985; Paper 5/1761