syn–anti-Photoisomerisation of Chelated Arylhydrazones of 1,2,3-Triketones: a Correction

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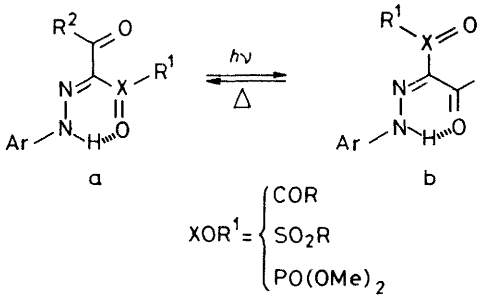
The exceptional u.v. spectroscopic and flash photolytic properties reported for the 4-methoxyphenylhydrazone derived from 4-nitrobenzoylacetone are erroneous and we propose a correction.

WE reported for the first time in 1976 [1] the photochromism of chelated 2-phenylhydrazones of 1,2,3-triketones and of substituted 1,2-diketones as a *syn–anti*-isomerisation around the C=N bond, a generalisation of the photochromic properties of enolised diaroylacetates and triketones previously described by us.[2] The lifetimes of the photogenerated species are between one minute and several days in anhydrous non-polar solvents (CCl_4, hexane) and from milliseconds to seconds in polar solvents (ROH, CH_3CN, and C_6H_5CN).



(1)

Truscott *et al.*, in a recent paper,[3] describe the behaviour of arylhydrazones derived from 1,2,3-triketones, as studied by laser flash photolysis (λ 347 nm). They confirm our results [1] for *syn-anti*-isomerism of the C=N bond for several compounds, except for the 4-methoxyphenylhydrazone derived from 4-nitrobenzoylacetone (1; X = C, R^1 = Me, $R^2 = 4\text{-}NO_2C_6H_4$, Ar = $4\text{-}MeOC_6H_4$) for which they find special behaviour. In contrast to other derivatives, only a very short-lived species is observed ($\lambda_{max.}$ 510 nm; $\tau_{\frac{1}{2}}$ 45 ns), with excited triplet characteristics, which are not shown by other hydrazones. According to the authors,[3] no *syn–anti*-isomerism takes place with this compound, as no other transient was observed.

Our results are not in accord with those claimed by Truscott *et al.*, who did not find a correct explanation for the particular behaviour of the 4-methoxyphenylhydrazone.

(1) The u.v. absorption spectrum of the 4-methoxyphenylhydrazone in contrast to values reported in ref. 3, is quite normal, $\lambda_{max.}$ 411 (hexane) or 415 nm (EtOH), with no $\lambda_{max.}$ at 312 and 330 nm as reported by Truscott *et al.*

(2) Irradiation by monochromatic light at 365 nm shifts the equilibrium from a to b: this is shown by u.v. examination of a hexane (5×10^{-5}M) solution of the 4-methoxyphenylhydrazone, with a bathochromic shift from 411 (a) to 421 nm (b). The thermal back reaction from b to a is very slow ($\tau_{\frac{1}{2}}$ 4 days) in non-polar solvents (hexane, CCl_4). I.r. spectroscopy of CCl_4 (10^{-3}M) solutions of the 4-methoxyphenylhydrazone shows the appearance of an intense absorption at 1 680 cm^{-1} (characteristic of tautomer b) with a progressive disappearance of the 1 652 cm^{-1} band (a was in 95% proportion at the thermal equilibrium). After 4 h irradiation at 365 nm, 90% of b is formed in the photostationary state. A flash photolytic study was performed easily only in polar solvents, with a half-life of 100 ms for b→a in absolute EtOH.

Our results refute the validity of Truscott's data concerning the 'exceptional' behaviour of the 4-methoxyphenylhydrazone. We suspect the occurrence of an impurity more hexane- or ethanol-soluble in Truscott's sample, which would be responsible for the u.v. spectrum reported and which was not observed in chloroform solutions by n.m.r. and i.r. spectroscopy.[4]

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REFERENCES

[1] P. Courtot, R. Pichon, and J. Le Saint, *Tetrahedron Letters*, 1976, 1181.

[2] P. Courtot, J. Le Saint, and R. Pichon, *Bull. Soc. chim. France*, 1975, 2538.

[3] J. McVie, A. D. Mitchell, R. S. Sinclair, and T. G. Truscott, *J.C.S. Perkin II*, 1980, 286.

[4] A. D. Mitchell and D. C. Nonhebel, *Tetrahedron*, 1979, **35**, 2013.