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PRELIMINARY NOTE

Photochemistry of 2-Fluoro-2-alkylcyclohexanones. Drastic Effect of Fluorine Substitution

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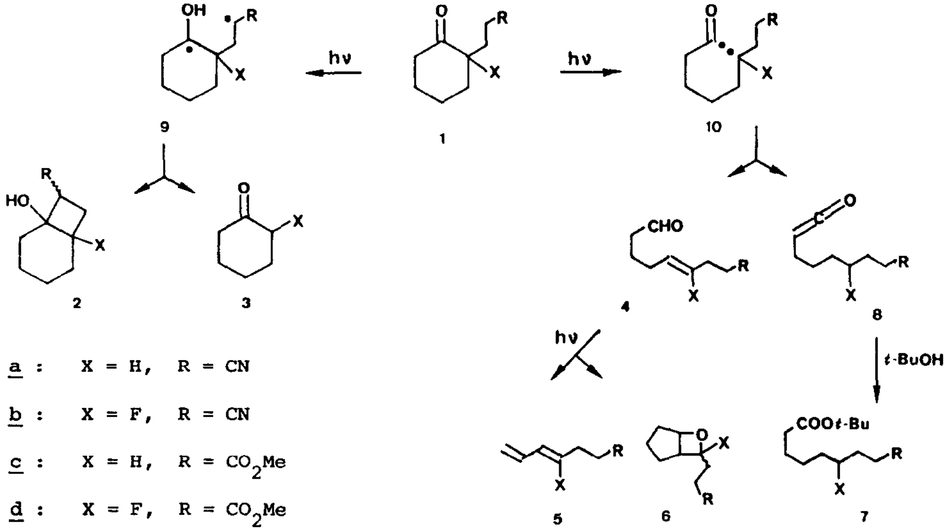
SUMMARY

In the photoreactions of 3-(2-oxocyclohexyl)-propionic acid derivatives 1 a pronounced effect of fluorine substitution is found on the ratio of a) Norrish II vs. Norrish I products; b) cyclization vs. cleavage of the Norrish II biradical; c) ketene vs. unsaturated aldehyde formation from the Norrish I biradical.

Norrish type I cleavage [1,2], e.g. 1 → 10 → 4 + 8, and type II photoprocesses [3], e.g. 1 → 9 → 2 + 3, are the two most important light induced reactions of cyclic ketones, both proceeding via biradicals as intermediates [4]. Little is known about competition between these two processes, the main reaction path for excited 2-alkylcyclohexanones apparently being the formation of type I biradicals [5,6]. We now report that a 2-fluoro substituent strongly influences the overall Norrish II vs. Norrish I product ratio, as well as the ratio of products formed from the Norrish II 1,4-biradical and the Norrish I 1,6-biradical, respectively.

Irradiation (λ= 300 nm) of 3-(2-oxocyclohexyl)-propionic acid derivatives 1a - 1d - synthesized from enamines of cyclohexanone or 2-fluorocyclohexanone [7] and acrylonitrile or methyl acrylate in 45-60% yield -

in t.BuOH affords products 2 - 7, analyzed by GC/MS, isolated by prep. GC and characterized by ^{1}H-NMR spectroscopy. Esters 7 result from reaction of ketene 8 with solvent; dienes 5 and oxabicycloheptanes 6 are formed by consecutive photoreactions of aldehydes 4. Except for esters 7, the formation of ketene 8 not being monitored, the same product distribution is observed in benzene as solvent.



a : X = H, R = CN

b : X = F, R = CN

c : X = H, R = CO_2Me

d : X = F, R = CO_2Me

Quantum yields for consumption of starting material [6], reflecting the combined behaviour of both, the excited states and the biradicals, are alike for all compounds 1 in both solvents indicating that the fluorine substituent does not exert a specific effect on either disproportionation with reverse hydrogen transfer of the Norrish II biradicals 9, or on the recombination of Norrish I biradicals 10, to 1. The product distribution given in the Table thus reflects the effect of fluorine on Norrish II vs. Norrish I reactivity of excited 1, on the relative rates of cyclization vs. cleavage of biradical 9 and on the partitioning of biradical 10 to 4 and 8, respectively. The values found for 1a and 1c are in very good agreement with those reported for 2-ethylcyclohexanone [5,6].

TABLE

Relative Percentage of Photoproducts and Quantum Yields for Consumption of 1a - 1d (10^{-1}M in t.BuOH).

	$\frac{2+3}{4+5+6+7}$ [a]	$\frac{2}{3}$ [b]	$\frac{4+5+6}{7}$ [c]	Φ_{-1} [d]
1a	30 / 70	0 / 100	60 / 40	0.19
1b	80 / 20	60 / 40	30 / 70	0.16
1c	25 / 75	0 / 100	60 / 40	0.12
1d	75 / 25	70 / 30	30 / 70	0.12

[a] Norrish II vs. Norrish I reactivity [b] Cyclization vs. cleavage of 9

[c] Unsaturated aldehyde (Enal) vs. ketene formation from 10

[d] Valerophenone as actinometer; error ± 0.02

The strongly enhanced Norrish II reactivity (intramolecular RH-reduction of a ketone [8]) reflects the lower reduction potential of alpha-fluoroketones - already known to favour intermolecular photoreduction [7] - as compared with the parent carbonyl compounds. Cyclobutanol 2 formation, not at all observed for 1a and 1c, becomes the major reaction of biradicals 9b and 9d. As conformational effects are important for the cleavage vs. cyclization ratio of Norrish II biradicals it is possible that an intramolecular OH - F hydrogen bond stabilizes 9 in a conformation unfavourable for cleavage to 3 [9]. Finally the result that fluorobiradicals 10b and 10d give much higher relative amounts of ketene 8 can be correlated to the higher rate constants for hydrogen abstraction from alkanes by trifluoromethyl than those for methyl radicals [10].

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