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PRELIMINARY NOTE

Photochemistry of 2-(Perfluoroalkyl)cycloalkanones

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SUMMARY

In an earlier study [1] we had compared the photochemical behaviour of 2-trifluoromethylcyclohexanone (1a) to that of the non-fluorinated parent ketone 2-methylcyclohexanone. Substitution of the methyl group on C(2) by a CF_3-group strongly enhances bimolecular reactions such as reduction product formation in 2-propanol or oxetane formation in the presence of alkenes. We now report preliminary results on monomolecular photochemical reactions of several 2-(perfluoroalkyl)cycloalkanones.

The predominant chemical process for excited cyclic ketones is the so-called α-cleavage, i.e. breaking of a C-C bond with formation of an acyl - alkyl diradical. Subsequent intramolecular hydrogen atom transfer gives either a ketene or an unsaturated aldehyde (enal). When the irradiation of the cycloalkanone is performed in an alcoholic solvent, the ketene is trapped as a carboxylic acid ester and the unsaturated aldehyde affords an acetal due to traces of acid present. The ratio of these α-cleavage products from cycloalkanones, i.e. ketene / enal in solvents as benzene or hydrocarbons, or in alcoholic solvents ester / acetal depends on energetic differences between transition states in the primarily formed acyl - alkyl diradical. For the few 2-alkylcyclopentanones and -cyclohexanones studied, these differences have been found to be rather insensitive to the presence of 2-substituents [2]. Furthermore studies of compounds with alkyl chains longer than methyl are complicated by competing Norrish-II (intramolecular H-abstraction by the carbonyl oxygen atom from the side chain) reactions [3].

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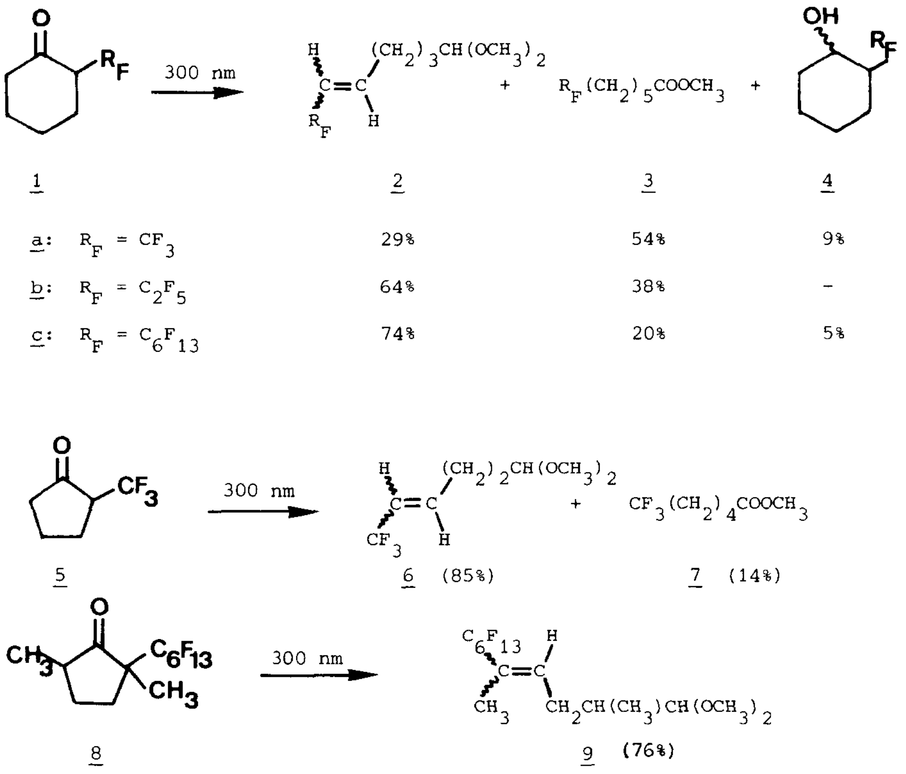
Irradiation (λ= 300 nm) of cyclohexanones $\underline{1}$ in benzene containing 10% methanol affords the two α-cleavage products $\underline{2}$ and $\underline{3}$ as well as traces of the corresponding cyclohexanols $\underline{4}$. Similarly irradiation of cyclopentanone $\underline{5}$ affords a mixture of the enal acetal $\underline{6}$ and the ester $\underline{7}$, while from cyclopentanone $\underline{8}$ acetal $\underline{9}$ is formed selectively (Scheme 1).



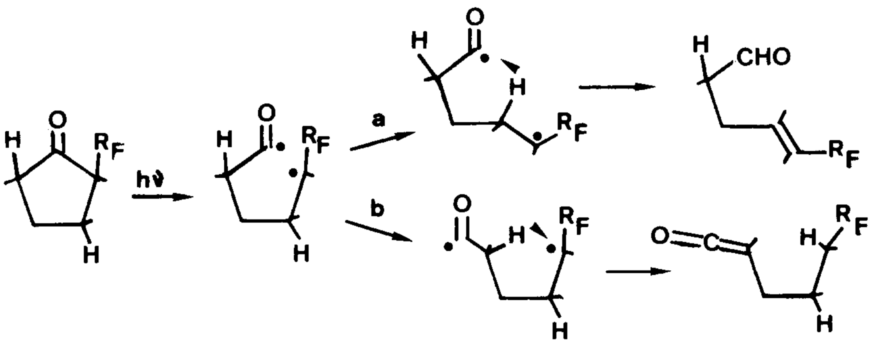
1	2	3	4
a: $R_F = CF_3$	29%	54%	9%
b: $R_F = C_2F_5$	64%	38%	-
c: $R_F = C_6F_{13}$	74%	20%	5%

Scheme 1

The assignment of the structures of the photoproducts is based on their ^{1}H-NMR - (Table 1) and mass spectra (Table 2). The unsaturated acetals are characterized by the chemical shift and the multiplicity of the olefinic & the $C\underline{H}(OR)_2$ protons, compounds $\underline{2}$ and $\underline{6}$ being present as mixtures of E and Z diastereomers as seen from the magnitude of the vicinal coupling constant of the olefinic protons (J = 16 and 10 Herz, respectively). In the mass spectra the radical ions of esters $\underline{3}$ and $\underline{7}$ undergo the well known

McLafferty rearrangement and fragmentation giving rise to base peaks m/e = 74 corresponding to the radical ion of the enol of methyl acetate.

Our results strongly suggest that the product ratio after α-cleavage is indeed a function of the perfluoroalkyl group on C(2), the relative amount of acetal increasing with the chain length. This can be explained assuming that enal formation (path a in Scheme 2) will be insensitive to the size of R_F, while ketene formation (path b) will certainly become less favourable with increasing chain length.



Scheme 2

TABLE 1

^{1}H-NMR data of photoproducts in $CDCl_3$

2	6.4 [a] and 6.0 [b] (m, 1H) and 5.6 (m, 1H), olefinic; 4.4 (t, 1H, CH(OR)$_2$); 3.3 (s, 6H, OCH_3); 2.2 (m, 2H); 1.7 - 1.5 (m, 4H).
3	3.7 (s, 3H, OCH_3); 2.35 (t, 2H); 2.1 (m, 2H); 1.9 - 1.5 (m, 6H).
4	4.3 and 3.7 (m, 1H, CHOH); 2.1 - 1.2 (m, 10H).
6	6.4 a) and 6.0 b) (m, 1H) and 5.6 (m, 1H), olefinic; 4.35 (t, 1H, CH(OR)$_2$); 3.35 (s, 6H, OCH_3); 2.2 (m, 2H); 1.8 - 1.6 (m, 2H).
7	3.7 (s, 3H, OCH_3); 2.35 (t, 2H); 2.1 (m, 2H); 1.6 (m, 4H).
9	6.1 (m, 1H, olefinic); 4.05 (d, 1H, CH(OR)$_2$); 3.35 (s, 6H, OCH_3); 2.3 (m, 2H); 1.9 (m, 1H); 1.8 (s, 3H, CH_3); 0.9 (d, 3H, CH_3).

[a] E - isomer [b] Z - isomer

TABLE 2

Mass spectroscopic data of photoproducts (spectra recorded at 70 eV) [a]

Acetals	M^+	m/e = 75 ($CH(OCH_3)_2^+$)
2a	212 (0.1%)	100 %
2b	262 (0.1%)	100 %
2c	462 (0.1%)	100 %
6	198 (0.9%)	100 %
9	476 (0.5%)	100 %
Esters	M^+	m/e = 74 ($CH_2{=}C(OH)OCH_3^+$)
3a	198 (0.1%)	100 %
3b	248 (0.1%)	100 %
3c	448 (0.9%)	100 %
Cyclohexanols		
4a	M^+ = 168 (9%)	base peak: 57
4c	M^+ = 418 (5%)	base peak: 41

[a] m/e = 69 (CF_3^+) usually < 10 %

Cyclohexanones 1a [1] and 1b & 1c [4] were synthesized according to the literature. 2-Trifluoromethylcyclopentanone (5) was prepared from N-cyclopent-1-enyl pyrrolidine and CF_3I in analogy to [4] in 10% yield, purification by chromatography on SiO_2 with CH_2Cl_2 as eluent, ^{1}H-NMR ($CDCl_3$): 2.85 (m, 1H), 2.35-1.90 (m, 6H); ^{13}C-NMR ($CDCl_3$): 209, 125(q), 51(q), 38, 24, 20 ppm; IR (CCl_4): 1750 cm^{-1}; MS: 152 (M^+), 55. 2-Perfluorohexyl-2,5-dimethylcyclopentanone (8) was prepared from 2,5-dimethylcyclopentanone [5] via its trimethylsilyl-enol ether (^{1}H-NMR in $CDCl_3$: 2.8-1.9(m, 4H), 1.6(s, 3H), 1.3(m, 1H), 1.0(d, 3H), 0.2(s, 9H)) and FITS-6 [6] in analogy to [7] in 14% yield, purification by chromatography on SiO_2 with ether/pentane 1:4 as eluent, ^{1}H-NMR ($CDCl_3$): 2.3-1.5(m, 5H), 1.25(s, 3H), 1.15(d, 3H); ^{13}C-NMR ($CDCl_3$): 212, 53(t), 45, 30, 27, 17, 14 ppm; IR (CCl_4): 1740 cm^{-1}; MS: 430 (M^+), 42.

Irradiations were performed in a Rayonet RPR-100 photoreactor with 300 nm lamps. Argon degassed solutions of 10^{-3} mol ketone in 10 ml benzene/MeOH 9:1 were irradiated for 30-50 h. Product analysis was performed by GC on a SE 30 capillary column or by 400 MHz ^{1}H-NMR of the crude photolysate. Isolation of products was done by preparative GC on a 8m 20% Reoplex 400 column, except for 2c and 3c which were obtained by chromatography on SiO_2 with ether/pentane 1:4 as eluent.

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