29. Photochemistry of Aliphatic Imines. The Photochemical Behaviour of Fluorinated *N*-Isopropylidenecyclohexylamines1)

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Summary

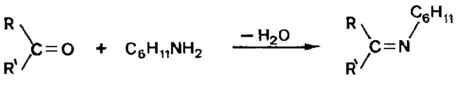
The cyclohexanimines of 1,3-difluoro-2-propanone and of 1,1,1-trifluoro-2-propanone have been synthesized. Their behaviour in acetone-photosensitized reactions is compared to that of the non-fluorinated parent compound.

In contrast to ketones [1], aliphatic imines [2] [3] are usually reluctant to undergo light-induced [2+2]-cycloadditions to unsaturated molecules, *e.g.* alkenes. We had observed that 6-fluoro-2-cyclohexenones [4] and 5-fluoro-2-cyclopentenones [5] react with olefins to form oxetanes selectively and we had also reported an analogous azetidine formation in the photocycloaddition of a fluorocyclohexenimine to 2,3-dimethyl-2-butene [6]. This last result led us to investigate simple fluorinated aliphatic imines, a class of compounds unknown up to now. An imine of a perfluorinated ketone [7] as well as the hydrazone [8], the oxime [8] and the *N,N*-dimethylhydrazone [9] of 1,1,1-trifluoro-2-propanone have been described in the literature. This latter ketone is also known to afford a cyclic trimer in the presence of aliphatic secondary amines [10] or of *t*-butylamine [11].

Addition of 1,3-difluoro-2-propanone or 1,1,1-trifluoro-2-propanone to cyclohexylamine in cold benzene and subsequent removal of water by azeotropic destillation afforded the imines **2** and **3** in reasonable yields (*Scheme 1*). The spectroscopic data of compounds **2** and **3** are summarized in the *Table*.

Irradiation ($\lambda > 280$ nm) of an Ar-degassed solution of **2** in acetone (or in D_6-acetone when monitoring the reaction by NMR.) leads to the selective formation

Scheme 1



2: R,R' = CH_2F
3: R=CH_3, R'=CF_3

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1) Reported at the VIIIth IUPAC-Symposium on Organic Photochemistry at Seefeld, Austria, July 1980.

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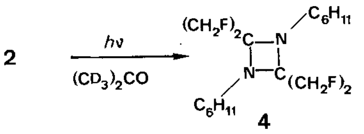
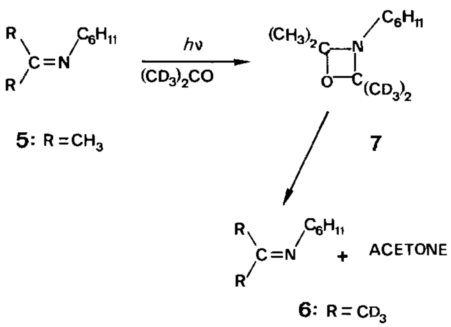
Table. *Spectroscopic data of imines* **2** *and* **3**

	UV. (C_6H_{12})	IR. (CCl_4)	MS.	^{1}H-NMR. ($CDCl_3$)	^{13}C-NMR. ($CDCl_3$)
2	260 (120)	1673	175 (11, M^+) 83 (100)	1.05-1.90 (*m*, 10 H); 3.37 (*m*, 1 H); 5.01 (*d*×*d*, J=47.0 and 1.0, 2 H); 5.15 (*d*, J=47.0, 2 H)	165 (*t*, J=18, *C*=N); 86 (*d*, J=174, CH_2F); 78 (*d*, J=174, CH_2F); 60 (s, CHN)
3	251 (155)	1665	193 (13, M^+), 83 (100)	1.10-1.85 (*m*, 10 H); 2.03 (*s*, 3 H); 3.42 (*m*, 1 H)	154 (*qa*, J=22, *C*=N); 120 (*qa*, J=283, CF_3); 60 (s, CHN); 36 (s, CH_3)

Scheme 2



Scheme 3



of a symmetric cyclic oligomer **4** *(Scheme 2)* as evidenced by the following spectroscopic arguments: *a)* disappearance of the (C=N)-absorption band in the IR. spectrum; *b)* disappearance of the UV.-absorption at 260 nm attributed to the n, π*-transition of the imine; *c)* the signals of the H- and C-atoms of the $C(CFH_2)_2$-group in the ^{1}H- and the ^{13}C-NMR. spectra in $CDCl_3$ are shifted to higher field [^{1}H-NMR.: one signal, 4.33 (*d*×*d*, J=46.5 and 2.0). - ^{13}C-NMR.: 84.0 (*d*, J=174, CH_2F); 72.2 (*t*, J=18 $(CH_2F)_2C$)]. The determination of the molecular weight of **4** failed, due to decomposition under different conditions of GC.-MS. analysis: as a matter of fact, **4** appeared to be stable only in solution, *e.g.* in pentane as solvent. We propose the structure of a 1,3-diazetidine for **4**, as in contrast, 1,2-diazetidines [12] and *s*-triazines [13] are known to be stable compounds, and because a higher molecular weight oligomer of **2** would most probably not be soluble in a solvent like pentane. The same compound **4** is again obtained selectively from **2**, when saturating the solution with isobutene or adding 2,3-dimethyl-2-butene to the reaction mixture, indicating that the photodimerization occurs more readily than photocycloaddition to an olefin.

The non-fluorinated parent compound **5** behaves differently. As expected, no structural changes are observed when irradiating **5** in acetone ($\lambda > 280$ nm) in the presence or absence of olefins. Instead, when the reaction is run in D_6-acetone, a rapid exchange between the CD_3-groups of acetone and the CH_3-groups of the imine is observed in the ^{1}H-NMR., and the hexadeuterioimine **6** [IR. (CCl_4): 1650] can be isolated in quantitative yield. No such reaction is observed in the dark. This suggests the light-induced formation of an unstable intermediate, possibly the oxazetidine **7**, which decomposes to **6** and acetone *(Scheme 3)*.

In contrast to **2** and **5** the trifluoroimine **3** is quite photostable[2]) in acetone (or in D_6-acetone) and no changes were observed when monitoring the reaction by NMR. spectroscopy, neither in the presence nor in the absence of olefins as isobutene or 2,3-dimethyl-2-butene.

We are now investigating the behaviour of a variety of imines from acyclic and cyclic fluorinated ketones under conditions of direct and sensitized irradiation in order to better understand the photochemistry of this class of compounds.

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Experimental Part

General. Absorptions in the IR. spectra are given in cm^{-1} and in the UV. spectra in nm (ε); chemical shifts in the NMR. spectra are given in ppm relative to TMS (=0 ppm) as internal standard (coupling constants J in Hz).

1. Starting materials. 1,3-difluoro-2-propanone and *N*-isopropylidenecyclohexylamine **5** were synthesized according to [14] and [15], respectively, 1,1,1-trifluoro-2-propanone was purchased from *Fluka AG.*

2. Preparation of imines **2** *and* **3**. The ketone (2.10^{-3} mol) was added to a solution of cyclohexylamine (3.10^{-3} mol) in 50 ml benzene at 0°. After stirring at this temperature for 2 h the mixture was refluxed for 12 h under a water separator. After evaporation of the solvent and excess amine the residue was distilled. Boiling points and yields: **2** (35-37°/0.2 Torr, 35%), **3** (36-39°/1 Torr, 28%).

3. Photolyses. Irradiations were carried out in Ar-degassed solutions by filtering the light of a 125 W mercury lamp through pyrex glass.

3.1. Irradiation of **2**. Complete conversion of **2** to **4** is achieved by irradiating 200 mg **2** in 1 ml $(CD_3)_2CO$ in a quartz NMR. tube for 2 h.

3.2 Irradiation of **5**. Complete conversion of **5** to **6** is achieved by irradiating 200 mg **5** in 2 ml $(CD_3)_2CO$ in a quartz NMR. tube for 36 h.

REFERENCES

[1] *G. Jones II,* in 'Organic Photochemistry', vol. 5, A. Padwa ed. M. Dekker 1981, p. 1.
[2] *A. Padwa,* Chem. Rev. *77,* 37 (1977).
[3] *A.C. Pratt,* Chem. Soc. Rev. *1977,* 63.
[4] *V. Desobry & P. Margaretha,* Helv. Chim. Acta *58,* 2161 (1975).
[5] *G. Vo Thi & P. Margaretha,* Helv. Chim. Acta *59,* 2236 (1976).
[6] *P. Margaretha,* Helv. Chim. Acta *61,* 1025 (1978).
[7] *W.J. Middleton & C.G. Krespan,* J. Org. Chem. *30,* 1398 (1965).
[8] *R.A. Shepard & P.L. Sciaraffa,* J. Org. Chem. *31,* 964 (1966).
[9] *F.J. Weigert,* J. Org. Chem. *37,* 1314 (1972).
[10] *M.M. Dhingra & K.R. Tatta,* Org. Magn. Reson. *9,* 23 (1977).
[11] *P. Margaretha,* unpublished results.
[12] *M.E. Landis, L.M. Bell, D.C. Madoux, J.C. Mitchell, J.M. Schmidt & J.A. Spencer,* J. Am. Chem. Soc. *102,* 837 (1980).
[13] *E.M. Smolin & L. Rapoport,* in 'The Chemistry of Heterocyclic Compounds', vol. 13, A. Weissberger, ed., Interscience 1959, p. 473.
[14] *E.D. Bergman & S. Cohen,* J. Chem. Soc. *1958,* 2259.
[15] *D.S.C. Black & N.A. Blackman,* Aust. J. Chem. *28,* 2547 (1975).

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[2]) After prolonged irradiation small amounts (5-10%) of a crystalline compound can be isolated. From chemical, spectroscopic and elementary analyses this (decomposition) product was found to be $C_6H_{11}NH_3^+HF_2^-$.