74. Photochemistry of 2-(Trifluoromethyl)cyclohexanone

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(16.I.84)

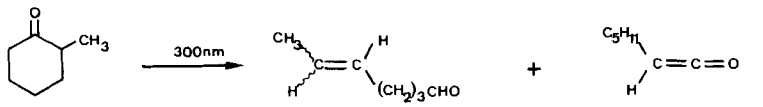
Summary

The photochemical behaviour of the title compound **1a** is compared to that of the non-fluorinated parent ketone 2-methylcyclohexanone (**1b**). Substitution of the CH_3-group on C(2) by a trifluoromethyl group strongly enhances *2H*- and *RH*-reduction product formation in cyclohexane or 2-propanol and oxetane formation in the presence of 2-methylpropene as olefinic component. Under all these conditions **1b** exclusively undergoes *α*-cleavage, a process observed for **1a** only in non-reducing solvents as benzene or *tert*-butyl alcohol.

We have recently shown that irradiation of *α*-fluoroketones in 2-propanol selectively affords the parent carbonyl compounds and that in non-reducing solvents as benzene or *t*-BuOH the fluoro-ketone and its parent compound exhibit a similar behaviour on excitation [1]. We now report results on comparative studies of light-induced reactions of 2-(trifluoromethyl)cyclohexanone (**1a**) and 2-methylcyclohexanone (**1b**) in these solvents.

Irradiation (λ = 300 nm) of **1b** in benzene or cyclohexane is known to afford the *α*-cleavage products 5-heptenal (**2**) and pentylketene (**3**) – trapped by alcohols to give esters – in a 2.3:1 ratio [2][3]. The quantum yields for product formation are 0.29 and 0.13, respectively [4]. No additional reduction products have been detected in 2-propanol [5] and no oxetanes were formed when the benzene solution of **1b** was saturated with 2-methylpropene *(Scheme 1)*.

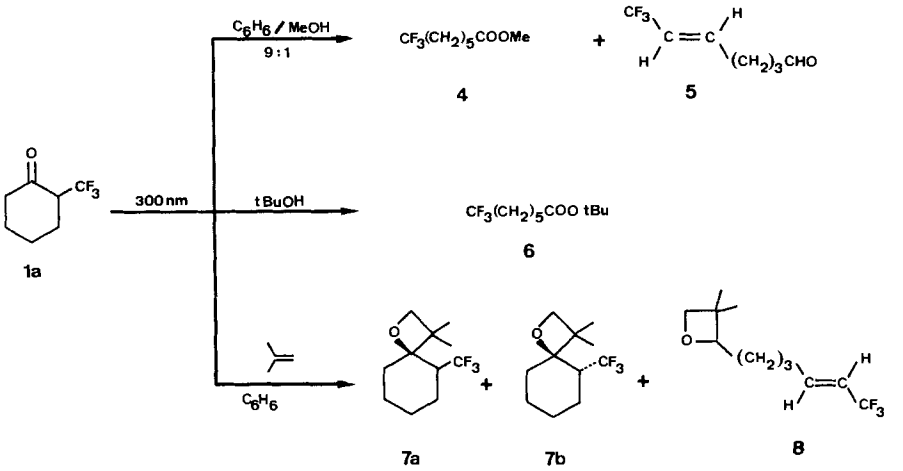
Scheme 1



1b **2** **(70%)** **3** **(30%)**

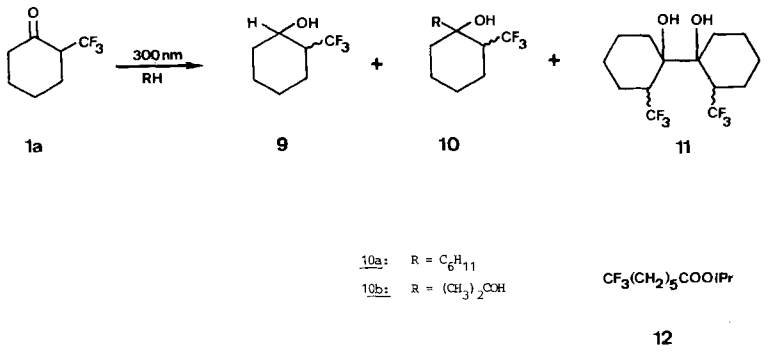
[1]) Part of the planned doctoral thesis, University of Hamburg.

Scheme 2



Irradiation (λ = 300 nm) of **1a** in benzene containing 10% MeOH afforded methyl 7,7,7-trifluoroheptanoate (**4**) and 7,7,7-trifluoro-5-heptenal (**5**) – this latter compound as a mixture of (*E*)- and (*Z*)-isomers – in a 2:1 ratio. Prolonged irradiation leads to destruction of the aldehyde, *e.g.* complete conversion of **1a** in *t*-BuOH affords *tert*-butyl 7,7,7-trifluoroheptanoate (**6**) selectively. Similarly, no products were detected by GC on prolonged irradiation of **1a** in pure benzene. On the other hand, when this solution was saturated with 2-methylpropene the three oxetanes **7a, 7b** and **8** were formed in a 4:5:1 ratio *(Scheme 2)*.

Scheme 3



In contrast, irradiation of **1a** in cyclohexane afforded *cis*- and *trans*-2-(trifluoromethyl)cyclohexanol (**9**), the *RH*-reduction product **10a** and pinacol **11.** No additional products were detected when using C_6H_{12}/C_6H_6/MeOH 8:1:1 as solvent. Similarly, in 2-propanol **9, 10b** and **11** represent the major products, only 2% of the isopropyl ester **12** being formed *(Scheme 3)*. The spectral data of the products are summarized in *Table 1* and the relative rates for the photodecomposition of **1a** and **1b** as well as the product distribution in the different solvents are given in *Table 2*.

Table 1. *Spectroscopic Data of Photoproducts from* **1a**

Compound	IR (CCl_4)	^{1}H-NMR ($CDCl_3$)	MS
4	1730 1135	–	198 (M^+) *74*
5[a])	–	9.75 (*t*, 1H); 6.35 (*m*, 1H); 5.70 (*m*, 1H); 2.5–1.4 (*m*, 6H)	166 (M^+) *44*
6	1730 1130	2.31 (*t*, 2H); 2.15 (*m*, 2H); 1.7–1.5 (*m*, 6H); 1.40 (*s*, 9H)	225 ($M^+ - CH_3$) *57*
7a[b])	1150	4.20 and 4.10 (*AB*, *J* = 5.4); 3.10 (*m*, 1H); 2.4–1.4 (*m*, 8H); 1.30 (*s*, 6H)	222 (M^+) *56*
7b[b])	1155	4.30 and 3.82 (*AB*, *J* = 5.4); 2.80 (*m*, 1H); 2.3–1.2 (*m*, 8H); 1.40 (*s*, 3H); 1.05 (*s*, 3H)	222 (M^+) *56*
8[a])	–	6.40 (*m*, 1H); 5.60 (*m*, 1H); 4.40 (*dd*, 1H); 4.30 and 4.10 (*AB*, *J* = 5.4); 2.15 (*m*, 2H); 1.8–1.3 (*m*, 4H); 1.25 (*s*, 3H); 1.20 (*s*, 3H)	192 ($M^+ - CH_2O$) *56*
9	3400 1130	4.35 (*m*, $1H_{eq}$) and 3.75 (*m*, $1H_{ax}$); 2.1–1.2 (*m*, 10H)	168 (M^+) *57*
10a	–	–	250 (M^+) *167*
10b	3650 3550 1155	–	208 (M^+) *59*
11	–	–	334 (M^+) *167*
12	1730 1140	5.02 (*m*, 1H); 2.30 (*t*, 2H); 2.10 (*m*, 2H); 1.7–1.4 (*m*, 6H); 1.30 (*d*, *J* = 6.5, 6H)	211 ($M^+ - CH_3$) *43*

[a]) Major compound is the (*E*)-isomer.
[b]) Structural assignment ambiguous.

Table 2. *Rates of Conversion of* **1a** *and* **1b** *and Product Ratios (GC) for* **1a** *in Different Solvents*

Solvent	k_{rel}		Product distribution (%)
	1a	**1b**	for **1a**
C_6H_6[a])	0.51	1 (Φ = 0.5 [2])	**4** (70), **5** (30)[b])
t-BuOH[c])	1.20	1.25	**6** (> 70)[d])
C_6H_{12}	1.75	1.02	**9** (50), **10a** (35), **11** (15)
i-PrOH	1.60	1.05	**9** (70), **10b** (15), **11** (13), **12** (2)

[a]) Containing 10% MeOH.
[b]) At 40% conversion of **1a**.
[c]) Containing 5% benzene.
[d]) At complete conversion of **1a**.

Comparison of the α-cleavage reaction of **1a** and **1b** shows that this process is only half as efficient for **1a** in benzene but of equal efficiency for both compounds in *t*-BuOH, and that the enal-to-ketene product ratios are inverted. These results reflect the

difference in behaviour of the acyl alkyl diradical intermediates ($CF_3\dot{C}HR$ *vs.* $CH_3\dot{C}HR$) regarding recombination to starting material and rearrangement to products [6].

Substitution of the CH_3-group on C(2) by a trifluoromethyl group reduces the potential of the ketone by 0.3 V [7], and therefore **1a** becomes a better oxidizing agent in its excited state as compared to **1b**. This feature is reflected in the ease of photoreduction of **1a** in cyclohexane or 2-propanol, solvents wherein **1b** again undergoes exclusively α-cleavage. In contrast to 2-fluorocyclohexanone the anion radical of **1a** does not eliminate F^-, and therefore the same product pattern is formed in 2-propanol as in C_6H_{12}. As for the oxetane forming [2 + 2] photocycloaddition, the CF_3-group on C(2) apparently exerts a similar effect as does fluorine itself [1][8]. Here again the α-cleavage for **1b** occurs efficiently enough as to prevent any bimolecular reaction.

Financial support by *Deutsche Forschungsgemeinschaft* and *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental Part

General. Absorptions in the IR spectra are given in cm^{-1}. Chemical shifts in the 400-MHz ^1H-NMR spectra are given in ppm relative to TMS (= 0 ppm) as internal standard. The GC/MS analyses were carried out on a *Varian MAT CH7* instrument using a 2-m column of 3% *SE30* on 80/100 *Suppelcoport*. Prep. GC was performed on 4-m columns of *a*) 10% SE30 and *b*) 10% FFAP on *Chromosorb G-AW-DMCS*.

Starting Materials. 2-Methylcyclohexanone (**1b**) was purchased from *Merck AG* and 2-(trifluoromethyl)aniline and 2-methylpropene from *Fluka AG*. All solvents used were of spectral grade.

2-(Trifluoromethyl)cyclohexanone (**1a**). A solution of 16.2 g (0.1 mol) 2-(trifluoromethyl)phenol (prepared in 35% yield by diazotization of 2-(trifluoromethyl)aniline and subsequent hydrolysis [9]) in 100 ml MeOH was hydrogenated at 150 atmospheres in the presence of 4.5 g *Raney*-Ni for 24 h at 170° [10]. After removal of the catalyst by filtration and distillation of the solvent through a *Vigreux* column the residue was dissolved in 100 ml CH_2Cl_2 and extracted 3× with 100 ml 2N NaOH. The org. phase was washed with H_2O and dried over $MgSO_4$. Distillation affords 4.5 g of a 7:1 mixture of 2-(trifluoromethyl)cyclohexanol (**9**) and 2-methylcyclohexanol, b.p. 55–60°/0.1 mm. This mixture of alcohols was added to a suspension of 8.5 g pyridiniumchlorochromate (PCC) in 60 ml CH_2Cl_2 and stirred at r.t. for 12 h. After addition of 50 ml pentane, filtration of the PCC over SiO_2 and evaporation of the solvent, the residue was chromatographed (SiO_2, CH_2Cl_2) to afford 2.3 g **1a** (14%), b.p. 73–75°/12 mm ([11]: 90–92°/30 mm).

Photolyses. Irradiations (λ = 300 nm) were performed in a *Rayonet RPR-100* photoreactor (lamp *a*) or with a 400 W medium pressure Hg-lamp and a *Pyrex* filter (lamp *b*). For analytical purposes degassed solutions of **1a** or **1b** (0.1M) were irradiated in a *merry-go-round* apparatus. The degrees of conversion were monitored by GC with undecane as internal standard.

In Benzene/MeOH 9:1. A solution of 33 mg **1a** in 2 ml solvent was irradiated for 16 h (lamp *a*). After removal of the solvent the residue was chromatographed (SiO_2, CH_2Cl_2) to afford a 1:2:2 mixture of **4/1a/5.**

In t-BuOH/benzene 95:5. A solution of 33 mg **1a** in 2 ml solvent was irradiated for 14 h (lamp *a*). *tert*-Butyl 7,7,7-trifluoroheptanoate **6** was isolated by prep. GC (column *a*, 30′ at 60°, 3°/min→140°).

In Benzene Saturated with 2-Methylpropene. A solution of 33 mg **1a** in 20 ml solvent was irradiated for 48 h (lamp *b*). ^1H-NMR and GC/MS analysis of the residue after evaporation of the solvent indicates the formation of *cis*- and *trans*-5-trifluoromethyl-3,3-dimethyl-1-oxaspiro[3.5]nonane **7a** and **7b** and of oxetane **8** in a 4:5:1 ratio. Chromatography (SiO_2, $MeCl_2$) affords 140 mg (30%) of the main component **7b.** Prep. GC (column *b*, isothermal 100°) allows to isolate each oxetane separately.

In Cyclohexane. A solution of 165 mg **1a** in 10 ml solvent was irradiated for 12 h (lamp *b*). Alcohols **9** and **10a** were isolated by prep. GC (column *a*, 30′ at 60°, 3°/min→140°). Under these conditions, **11** could not be isolated.

In 2-Propanol. Irradiation- and prep. GC conditions as above for cyclohexane affords alcohol **9,** ester **12** and alcohol **10b.** Under these conditions **11** could not be obtained.

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