

74. Photochemistry of 2-(Trifluoromethyl)cyclohexanone

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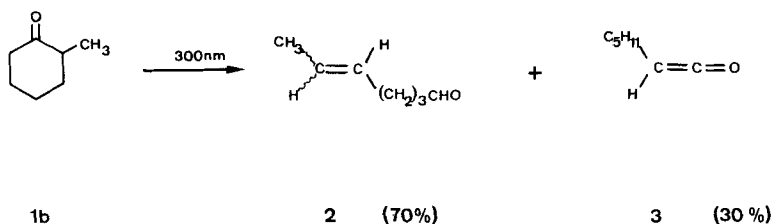
Summary

The photochemical behaviour of the title compound **1a** is compared to that of the non-fluorinated parent ketone 2-methylcyclohexanone (**1b**). Substitution of the CH₃-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.

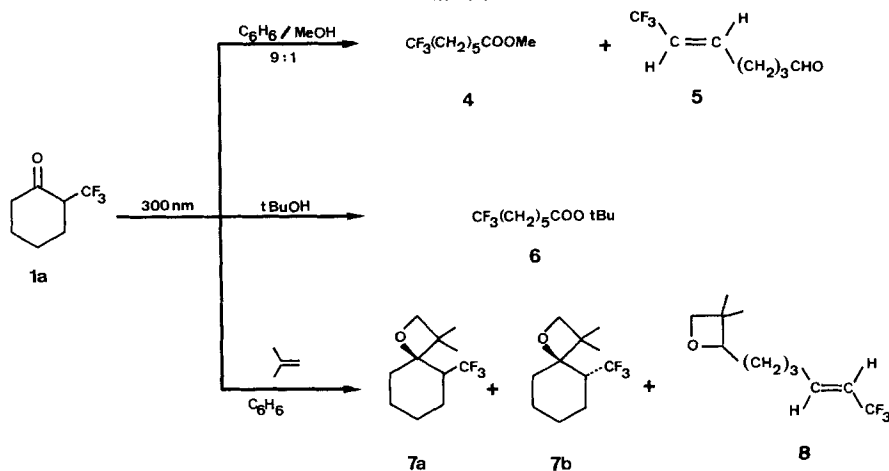
Irradiation ($\lambda = 300$ nm) of **1b** in benzene or cyclohexane is known to afford the α -cleavage products 5-heptenal (**2**) and pentylketene (**3**) – trapped by alcohols to give esters – in a 2.3:1 ratio [2][3]. The quantum yields for product formation are 0.29 and 0.13, respectively [4]. No 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



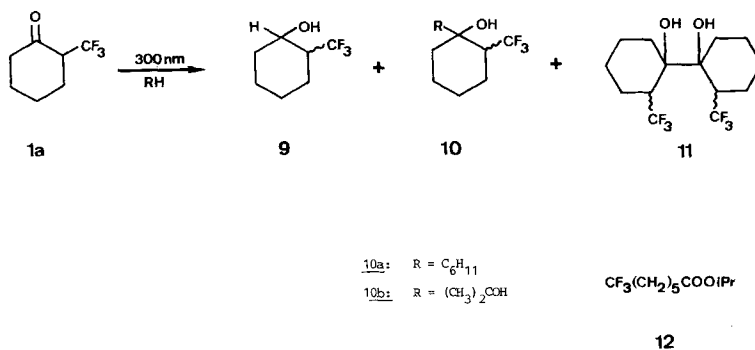
¹⁾ Part of the planned doctoral thesis, University of Hamburg.

Scheme 2



Irradiation ($\lambda = 300\text{ nm}$) 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 $\text{C}_6\text{H}_{12}/\text{C}_6\text{H}_6/\text{MeOH}$ 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 (<i>M</i> ⁺) 74
5^{a)}	—	9.75 (<i>t</i> , 1H); 6.35 (<i>m</i> , 1H); 5.70 (<i>m</i> , 1H); 2.5–1.4 (<i>m</i> , 6H)	166 (<i>M</i> ⁺) 44
6	1730 1130	2.31 (<i>t</i> , 2H); 2.15 (<i>m</i> , 2H); 1.7–1.5 (<i>m</i> , 6H); 1.40 (<i>s</i> , 9H)	225 (<i>M</i> ⁺ – CH ₃) 57
7a^{b)}	1150	4.20 and 4.10 (<i>AB</i> , <i>J</i> = 5.4); 3.10 (<i>m</i> , 1H); 2.4–1.4 (<i>m</i> , 8H); 1.30 (<i>s</i> , 6H)	222 (<i>M</i> ⁺) 56
7b^{b)}	1155	4.30 and 3.82 (<i>AB</i> , <i>J</i> = 5.4); 2.80 (<i>m</i> , 1H); 2.3–1.2 (<i>m</i> , 8H); 1.40 (<i>s</i> , 3H); 1.05 (<i>s</i> , 3H)	222 (<i>M</i> ⁺) 56
8^{a)}	—	6.40 (<i>m</i> , 1H); 5.60 (<i>m</i> , 1H); 4.40 (<i>dd</i> , 1H); 4.30 and 4.10 (<i>AB</i> , <i>J</i> = 5.4); 2.15 (<i>m</i> , 2H); 1.8–1.3 (<i>m</i> , 4H); 1.25 (<i>s</i> , 3H); 1.20 (<i>s</i> , 3H)	192 (<i>M</i> ⁺ – CH ₂ O) 56
9	3400 1130	4.35 (<i>m</i> , 1H _{eq}) and 3.75 (<i>m</i> , 1H _{ax}); 2.1–1.2 (<i>m</i> , 10H)	168 (<i>M</i> ⁺) 57
10a	—	—	250 (<i>M</i> ⁺) 167
10b	3650 3550 1155	—	208 (<i>M</i> ⁺) 59
11	—	—	334 (<i>M</i> ⁺) 167
12	1730 1140	5.02 (<i>m</i> , 1H); 2.30 (<i>t</i> , 2H); 2.10 (<i>m</i> , 2H); 1.7–1.4 (<i>m</i> , 6H); 1.30 (<i>d</i> , <i>J</i> = 6.5, 6H)	211 (<i>M</i> ⁺ – 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	<i>k</i> _{rel}		Product distribution (%) for 1a
	1a	1b	
C ₆ H ₆ ^{a)}	0.51	1 (<i>φ</i> = 0.5 [2])	4 (70), 5 (30) ^{b)}
<i>t</i> -BuOH ^{c)}	1.20	1.25	6 (> 70) ^{d)}
C ₆ H ₁₂	1.75	1.02	9 (50), 10a (35), 11 (15)
<i>i</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 ($\text{CF}_3\dot{\text{C}}\text{HR}$ vs. $\text{CH}_3\dot{\text{C}}\text{HR}$) 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.

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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 $\times$ with 100 ml 2*N* 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. $55\text{--}60^\circ/0.1$ 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. $73\text{--}75^\circ/12$ mm ([11]: $90\text{--}92^\circ/30$ mm).

Photolyses. Irradiations ($\lambda = 300$ 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** (0.1*M*) 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° , $3^\circ/\text{min} \rightarrow 140^\circ$).

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° , $3^\circ/\text{min} \rightarrow 140^\circ$). 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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