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PHOTOCHEMISTRY OF 6-TRIFLUOROMETHYL-4,4-DIMETHYL-2-CYCLOHEXENONE

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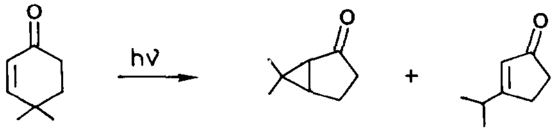
SUMMARY

The photochemical behaviour of the title compound, newly synthesized in four steps from 4,4-dimethylcyclohexanone, is compared to that of 4,4-dimethyl- and 4,4,6-trimethyl-2-cyclohexenone. All three enones undergo rearrangement to bicyclo[3.1.0]hexan-2-ones and 3-isopropyl-2-cyclopentenones in benzene, t.butanol and acetonitrile, but only the CF_3-enone is also reduced to the saturated ketone in the latter two solvents.

INTRODUCTION

In previous papers we have communicated that substitution of a CH_3 by a CF_3 group on C(2) of cycloalkanones [1,2] and on C(6) of 2-cyclohexenone [3] enhances the formation of photoreduction (electron transfer) products [4]. We now report results on photoreactions of 6-trifluoromethyl-4,4-dimethyl-2-cyclohexenone (1a) and compare them with those of 4,4,6-trimethyl- and 4,4-dimethyl-2-cyclohexenone, 1b and 1c, respectively. In contrast to other 2-cyclohexenones which afford tricyclic dimers on irradiation [5], 4,4-dialkyl-2-cyclohexenones, e.g. 1c, undergo the socalled lumiketone rearrangement to bicyclo[3.1.0]hexan-2-ones 2 and 2-cyclopentenones 3, albeit with low quantum efficiencies [6].



1c **2c** **3c**

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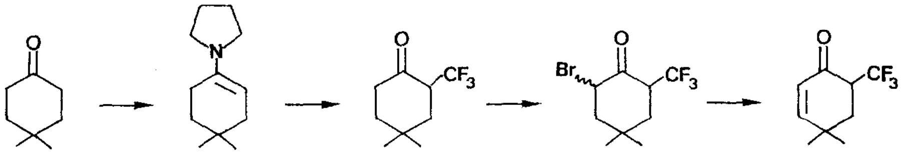
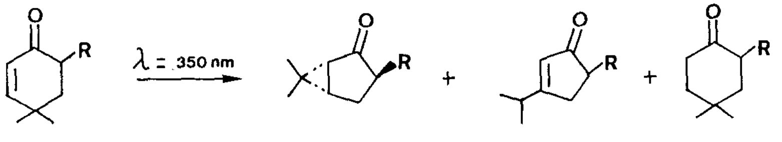
RESULTS AND DISCUSSION

The previously unknown title compound 1a was synthesized from 4,4-dimethylcyclohexanone (4) [7] in four steps in 25% overall yield. Condensation of 4 with pyrrolidine afforded enamine 5 which was converted to 2-trifluoromethyl-4,4-dimethylcyclohexanone (6) according to [8]. Bromination of 6 gave a 3:2 mixture of cis- and trans bromoketones 7 which were finally dehydrobrominated to 1a. Enones 1b and 1c were synthesized according to [9] and [10], respectively.



4 5 6 7 1a

Irradiation (λ = 350 nm) of enones 1 in benzene, t.butanol or acetonitrile afforded lumiketones 2 and cyclopentenones 3. In t.butanol and acetonitrile 6 was also formed from 1a. On prolonged irradiation cyclopentenones 3 underwent consecutive photoreactions. Lumiketones 2 were characterized by ^{1}H-NMR (bridgehead CHCO as doublet, J = 5 - 6 Hz) and by MS (low intensity molecular ion, base peak m/z = 82, corresponding to CH_2=CH-CH=$(CH_3)_2$, formed by C(1)-C(2) bond cleavage, ketene elimination and cyclopropane bond cleavage). Cyclopentenones 3 show signals for the olefinic proton and the isopropyl group in the ^{1}H-NMR spectrum as well as high intensity molecular ions in the MS. GC retention times for 3 on a SE 30 capillary column were always higher than those for 2. Relative rates of conversion of starting material are given in Table 1, product distributions in the different solvents - extrapolated to 0% conversion - in Table 2. The ^{1}H-NMR data for all new compounds is summarized in Table 3 and the mass spectroscopic data in Table 4.



1 2 3 6 (R=CF_3)

a: R = CF_3 b: R = CH_3 c: R = H

TABLE 1

Relative rates of conversion of cyclohexenones 1a-1c (10^{-1}M) on irradiation (λ= 350 nm)

	C_6H_6	t.BuOH	CH_3CN
1a	0.085	0.26	0.265
1b	0.15		
1c	0.34	1.0 [a]	

[a] Quantum yield for 1c in t.BuOH = 0.014 [11]

TABLE 2

Product distribution - extrapolated to 0% conversion - in irradiations of 1a-1c (10^{-1}M), λ = 350 nm

	C_6H_6	t.BuOH	CH_3CN
1a	2a(37%) 3a(63%)	2a(31%) 3a(47%) 6(22%)	2a(39%) 3a(47%) 6(14%)
1b	2b(38%) 3b(62%)	2b(42%) 3b(58%)	2b(49%) 3b(51%)
1c	2c(62%) 3c(38%)	2c(52%) 3c(48%)	2c(65%) 3c(35%)

From the results summarized in Tables 1 & 2 it becomes evident that both CH_3 and CF_3 groups on C(6) exert similar effects on the photorearrangement of 4,4-dimethyl-2-cyclohexenones, by a) slowing down the overall reaction rate, and b) shifting the product ratio 2:3 towards higher relative amounts of cyclopentenones 3. It has been stated that the lumiketone rearrangement 1 → 2 requires either a concerted mechanism, or a stepwise mechanism involving short lived diradical intermediates and that the efficiency of this rearrangement is determined solely by the relative topology of triplet and ground state surfaces of the twisted enone, formed after crossing from the singlet to the triplet manifold [6]. Whereas the lowering of the quantum efficiencies - as compared to 1c - is most probably due to conformational changes in the excited enone by the substitutents on C(6), the important change in the product ratio 2:3 by these substituents makes common (diradical) intermediates, e.g. 8 and 9, to both products 2 and 3 more probable. The stereoselectivities found in some lumiketone rearrangements do not rule out diradical intermediates, because rotation barriers for biradicals may exceed those for free radicals, and strain-free cyclizations to 5-membered rings generally enjoy large rate advantages over their intermolecular counterparts [12]. Furthermore 8 behaves exactly as expected for a 5-hexenyl radical, a species which is known [13,14] to a) undergo ring closure in the exo mode to give five membered rings selectively, and b) afford trans-disubstituted 5-membered rings, e.g. 9, when bearing a substituent on C(2). It is therefore not surprising that from 1a or 1b only one lumiketone is formed, respectively.

1 8 9

As for 2-trifluoromethylcyclohexanone [1,2] or 6-trifluoromethyl-2-cyclohexenone [3] the specific effect of the CF_3 group is again increased reduction product formation, i.e. 15-20% 6 from 1a vs. less than 3% 2,4,4-trimethylcyclohexanone from 1b or 4 from 1c in t.butanol or acetonitrile. The similarity in behaviour of 1a and 1b in benzene reflects the well known lack of reactivity of this solvent in reducing excited carbonyl compounds.

TABLE 3

^{1}H-NMR Spectroscopic data in $CDCl_3$

1a: 6.70 (dd, J = 10.2, 2.2) H-C(3); 5.85 (d, J = 10.2) H-C(2); 3.23 (ddq, J = 13.4, 5.0, 8.4) H_a-C(6); 2.12 (ddd, J = 13.4, 5.0, 2.2) H_e-C(5); 2.01 (t, J = 13.4) H_a-C(5); 1.26 & 1.24 (s, CH_3)

2a: 3.20 (ddq, J = 12.8, 9.4, 9.9) H-C(3); 2.57 (ddd, J = 14.2, 12.8, 7.2) H_a-C(4); 1.97 (ddd, J = 14.2, 9.4, 1.8) H_e-C(4); 1.88 (ddd, J = 7.2, 5.5, 1.8) H-C(5); 1.82 (d, J = 5.5) H-C(1); 1.18 & 1.12 (s, CH_3)

3a: 5.95 (s) H-C(2); 3.15 (ddq, J = 7.4, 3.4, 10.2) H-C(5); 2.91 (dd, J = 19.0, 7.4) and 2.75 (dd, J = 19.0, 3.4) H-C(4) 2.65 (sept., J = 7.0); 1.32 (d, J = 7.0, CH_3)

(continued)

TABLE 3 (cont.)

6: 3.21 (ddq, J = 13.0, 5.2, 8.0) H_a-C(2); 2.49 (dt, J = 6.8, 13.9) H_a-C(6); 2.35 (ddd, J = 13.9, 4.5, 3.0) H_e-C(6); 1.98 (ddd, J = 13.5, 5.2, 3.0) H_e-C(3); 1.82-1.65 (m, 3H); 1.25 & 1.10 (s, $C\underline{H}_3$)

7a: 4.75 (ddd, J = 13.6, 6.0, 0.5) H_a-C(2); 3.35 (dddq, J = 13.0, 5.4, 0.5, 7.6) H_a-C(6); 2.55-1.75 (m, 4H); 1.15 & 1.10 (s, $C\underline{H}_3$)

7b: 4.45 (dd, J = 5.6, 3.4) H_e-C(2); 3.90 (ddq, J = 13.2, 5.0, 8.0) H_a-C(6); 2.55-1.75 (m, 4H); 1.45 & 1.35 (s, $C\underline{H}_3$)

TABLE 4

Mass spectroscopic data (70 eV electron impact spectra)

1a: 192 (M^+, 15%), 96 ($M^{+\cdot}$ - $CF_3CH{=}CH_2$, 100%), 69 (CF_3^+, 7%)

2a: 192 (M^+, 12%), 82 (M^+ - CF_3CHCO, 100%), 69 (CF_3^+, 12%)

2b: 138 (M^+, 7%), 82 (M^+ - CH_3CHCO, 86%), 67 (82 - CH_3, 100%)

2c: 124 (M^+, 14%), 82 (M^+ - CH_2CO, 100%), 67 (93%)

3a: 192 (M^+, 63%), 150 (M^+ - C_3H_6, 69%), 82 (100%), 69 (CF_3^+, 18%)

3b: 138 (M^+, 52%), 67 (100%)

3c 124 (M^+, 41%), 82 (M^+ - C_3H_6, 100%)

6: 194 (M^+, 34%), 139 (M^+ - 55, 43%), 69 (CF_3^+, 30%), 55 (100%)

7a: 274 & 272 (M^+, 30%), 69 (CF_3^+, 100%)

7b 274 & 272 (M^+, 23%), 69 (CF_3^+, 100%)

EXPERIMENTAL

General

Chemical shifts in the 400-MHz ^1H-NMR spectra are given in ppm relative to TMS (coupling constants J in Hz). Analytical GC was performed on a SE 30 capillary column. Preparative GC separations were run on a 10% QF1 column.

Starting Materials

4,4,6-Trimethyl-2-cyclohexenone (1b) [9] and 4,4-dimethyl-2-cyclohexenone (1c) [10] were synthesized according to the literature.

(a) Preparation of 1-pyrrolidino-4,4-dimethylcyclohexene (5)

A solution of 15.1 g (0.12 mol) 4,4-dimethylcyclohexanone (4) [7] and 10 g (0.14 mol) pyrrolidine in 30 ml toluene containing 30 mg p.toluenesulphonic acid was refluxed until the calculated amount of water had separated on a Dean-Stark trap. After washing with water, drying over $MgSO_4$ and evaporation of the solvent, distillation afforded 16.1 g (75%) 5, b.p. 118°/12 mm, IR (film): 3050, 3030, 1640 cm^{-1}.

(b) Preparation of 2-trifluoromethyl-4,4-dimethylcyclohexanone (6)

To a solution of 15 g (0.084 mol) 5 and 10.8 g (0.084 mol) ethyldiisopropylamine in 150 ml pentane at -50° were added 17 g CF_3I. Work-up according to [8] , chromatography (SiO_2, CH_2Cl_2) and subsequent distillation afforded 12.6 g (77%) 6, b.p. 96°/12mm, IR (film): 1720 cm^{-1}.

(c) Preparation of cis- and trans 2-bromo-6-trifluoromethyl-4,4-dimethylcyclohexanone (7a) & (7b)

To a solution of 7.44 g (0.038 mol) 6 in 160 ml CCl_4 at 40° is slowly added a soln. of 6 g (0.038 mol) bromine in 10 ml CCl_4. After evaporation of the solvent the solid residue was recrystallized from ether. Yield: 9.6 g (92%), m.p. 70-73°. According to ^1H-NMR the ratio of 7a to 7b was 3:2.

(d) Preparation of 6-trifluoromethyl-4,4-dimethyl-2-cyclohexenone (1a)

8.2 g (0.03 mol) of the mixture of 7a and 7b and 12 g (0.12 mol) $CaCO_3$ were heated under N_2 in 150 ml dimethylacetamide at 120° for 4h. After filtration, pouring into 600 ml water, extraction with pentane, drying over $MgSO_4$ and evaporation of the solvent, distillation afforded 5.2 g (90%) 1a, b.p. 81°/12mm, IR(film): 1690 cm^{-1}; UV (C_6H_{12}): 309 nm, ε = 28 and 219 nm, ε = 13700; ^{13}C-NMR ($CDCl_3$): 191 (s), 159 (d), 126 (d), 125 (q, J_{CF} = 278 Hz), 47 (q, J_{CF} = 25 Hz), 36 (t), 33 (s), 30 (q), 25 (q).

Photolyses

These were performed in a Rayonet RPR-100 photoreactor using 350 nm lamps. All solutions were Argon-degassed. For analytical runs (determination of the relative reaction rates) 1 ml of a 10^{-1}M solution of enones 1a - 1c was irradiated and the reaction monitored by GC using undecane as internal standard. For preparative purposes 25 ml of 10^{-1}M solns. of 1a - 1c were irradiated for 50 - 100h (monitoring by GC); all products were isolated by prep. GC as colourless liquids.

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