

Photochemistry of 2-Methyl-2-trifluoromethyl- and 2,2-Bis(trifluoromethyl)-3(2H)-furanone

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The behaviour of 2-methyl-2-trifluoromethyl-3(2H)-furanone (**1b**) and 2,2-bis(trifluoromethyl)-3(2H)-furanone (**1c**) is compared to that of the parent dimethyl compound **1a** for the following light-induced reactions: (a) cyclodimerization, (b)

[2 + 2] cycloaddition to 2,3-dimethyl-2-butene, and (c) reductive (RH) addition to 2-propanol. A pronounced acceleration due to the exchange of CH₃ against CF₃ is observed in this last reaction; the mechanistic aspects are discussed.

The presence of a CF₃ substituent at C- α of cyclic ketones or C- α' of cyclic α,β -unsaturated ketones has a pronounced effect on the photoreactivity of these carbonyl compounds. Thus, for saturated ketones, product distributions from α cleavage^{1,2)} are affected. For 6-substituted 4,4-dimethyl-2-cyclohexenones both intermolecular reactions, e.g. the lumiketone rearrangement³⁾, and intramolecular reactions, e.g. photoaddition vs. photocyclization to alkenes⁴⁾, are strongly influenced. A qualitative comparison of the photochemical behaviour of 6-trifluoromethyl-2-cyclohexenone and 6-methyl-2-cyclohexenone⁵⁾ indicated that higher yields of reduction products are obtained from the trifluoromethyl than the methyl enone in 2-propanol as solvent.

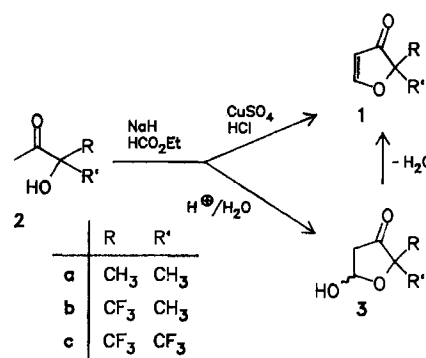
Heterocyclic five-membered enones as 3(2H)-furanones, e.g. 2,2-dimethyl-3(2H)-furanone⁶⁻⁸⁾ (**1a**), 3(2H)-thiophenones^{9,10)}, and 2,3-dihydro-1H-pyrrole-3-ones¹¹⁾, turned out to be very good model compounds for studying mechanistic aspects of the photochemistry of 2-cyclopentenone itself. We now report on comparative studies of the photochemical behaviour of the newly synthesized trifluoromethylfuranones **1b** and **1c** with that of the parent dimethyl furanone **1a**.

Results

The previously unknown furanones **1b** and **1c** were synthesized in analogy to **1a**, i.e. from the corresponding 3-alkyl-3-hydroxy-2-butanones **2** by a one-pot formylation, cyclization, and dehydration sequence⁶⁾. Attempted isolation of the intermediate cyclic hemiacetals **3** was successful only for **3b** (obtained as a 1:9 mixture of diastereoisomers **3b_c** and **3b_i**) but not for **3c**, which dehydrates to **1c** both during distillation or on SiO₂ or Al₂O₃. 3-Hydroxy-4,4,4-trifluoro-3-trifluoromethyl-2-butanone (**2c**) was obtained from hexafluoroacetone cyanohydrin in analogy to the published preparation of **2b** from trifluoroacetone cyanohydrin¹²⁾ (Scheme 1).

Irradiation ($\lambda = 350$ nm) of 10⁻¹ M solutions of **1** in the presence of a tenfold molar excess of 2,3-dimethyl-2-butene in C₆H₆ affords the 2-oxabicyclo[3.2.0]heptan-4-ones **4** selectively (diastereoisomers **4b_c** and **4b_i** were separated by

Scheme 1

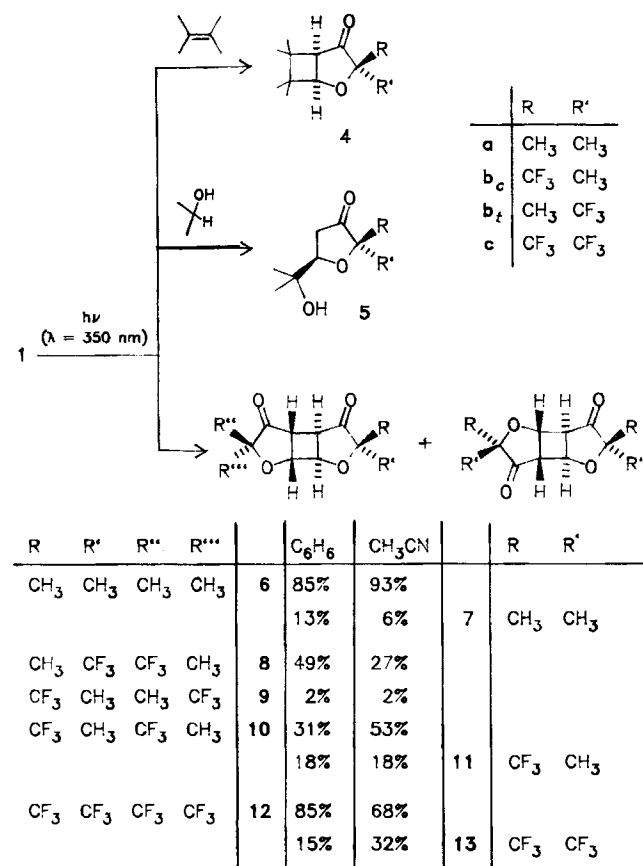


column chromatography). Photolysis of 10⁻¹ M solutions of **1** in 2-propanol affords 5-(1-hydroxy-1-methyl)ethyl-4,5-dihydrofuranones **5** as only products (diastereoisomers **5b_c** and **5b_i** were not completely separated by chromatography). Finally, irradiation of 10⁻¹ M **1a** in C₆H₆ or CH₃CN affords tricyclic dimers **6**, **7** with *anti* configuration and a third dimer in 2% yield of *syn* configuration but of unknown constitution; while **1b** gives dimers **8–11**, and **1c** provides dimers **12** and **13** under these conditions, the product distributions (analysis by NMR and GC) vary with the solvent used (Scheme 2).

The spectroscopic data (¹H-NMR, MS) and α values (separation factors determined by enantioselective gas chromatography¹³⁾) of the photoproducts are summarized in Table 1.

Comparative relative rates of product formation from **1a**, **1b**, and **1c** were measured by using a merry-go-round setup in the photolyses (and GC analysis against an internal standard). For the cycloaddition to 2,3-dimethyl-2-butene (formation of oxabicycloheptanones **4**) the values obtained were $k_{rel} = 1.0:1.1:1.1$ and for the reductive (RH) addition to 2-propanol (formation of **5**) $k_{rel} = 1.0:8.6:10.8$.

Scheme 2



Discussion

Concerning the structures and the yields of the photoproducts, the furanones **1a–1c** behave very similarly in the three reactions investigated. On irradiation of 10^{-1} M **1** in both benzene and acetonitrile head-to-head dimers are formed preferentially, the ratio of head-to-head to head-to-tail dimers being higher in acetonitrile than in benzene for **1a** (**6**:**7** = 6.5:1.0 in C₆H₆ and 16:1 in CH₃CN), alike for **1b** [**8** + **9** + **10**]:**11** = 4.5:1.0 in both solvents] and inverse for **1c** (**12**:**13** = 5.6:1.0 in C₆H₆ and 2.1:1.0 in CH₃CN). Cycloadducts **4** and RH addition products **5** are formed selectively in the respective reactions. A downfield shift of about 0.15 ppm and 0.13 ppm per CF₃ group is observed in the ¹H-NMR spectra for the *CHCO* and the *CHO* protons, respectively. For hemiacetals **3b** and for photoproducts **4b**, **5b**, **8**, and **9**, the diastereoisomer with the *CHO* proton resonating at lower field was arbitrarily assigned the *trans* configuration, i.e., this hydrogen atom is *cis* to the CF₃ group.

Important differences are found for the particular relative rates of product formation from **1**: on the one hand almost no effect due to CF₃ vs. CH₃ is observed in the cycloaddition to 2,3-dimethyl-2-butene; on the other a strong acceleration ($k_{\text{rel}} = 1.0:8.6:10.8$) is observed for the formation of **5a–5c**, respectively. Clearly the replacement of CH₃ by CF₃ in **1** has a pronounced influence on the photoreduction of these compounds. We have recently proposed¹⁴ that both inter-

Tab. 1. ¹H-NMR^{a)} and MS^{b)} data and α^c values of photoproducts

Compound	¹ H-NMR
4a ⁷⁾	4.12 and 2.78 (AB, $J = 4.8$), 1.34, 1.33, 1.21, 1.11, 1.06, and 1.02 (s, CH ₃)
4b_c	4.25 and 2.84 (AB, $J = 5.6$), 1.45, 1.15, 1.13, 1.07, and 1.05 (CH ₃)
4b_t	4.35 and 2.90 (AB, $J = 5.6$), 1.45, 1.13, 1.11, 1.02, and 1.00 (CH ₃)
4c	4.54 and 2.96 (AB, $J = 6.2$), 1.18, 1.15, 1.08, and 1.05 (CH ₃)
5a	4.07 (dd, $J = 6.0, 10.3$), 2.63 (dd, $J = 10.3, 18.3$), 2.40 (dd, $J = 6.0, 18.3$), 1.37, 1.32, 1.31, and 1.25 (CH ₃)
5b_c	4.12 (dd, $J = 6.0, 11.0$), 2.86 (dd, $J = 11.0, 18.4$), 2.52 (dd, $J = 6.0, 18.4$), 1.38, 1.24, and 1.18 (CH ₃)
5b_t	4.30 (dd, $J = 7.3, 7.6$), 2.75 (dd, $J = 7.6, 18.4$), 2.61 (dd, $J = 7.3, 18.4$), 1.45, 1.24, and 1.18 (CH ₃)
5c	4.43 (dd, $J = 6.4, 10.0$), 2.98 (dd, $J = 10.0, 18.8$), 2.73 (dd, $J = 6.4, 18.8$), 1.42 and 1.22 (CH ₃)
6 ⁷⁾	4.52 and 3.21 (AA'BB', $J_{AA'} = 4.4, J_{AB} = 4.8, J_{AB'} = 0.7, J_{BB'} = 0.1$), 1.40 and 1.02 (CH ₃)
7	4.73 and 3.29 (AA'BB', $J_{AA'} = 2.1, J_{AB} = 5.6, J_{AB'} = 1.6, J_{BB'} = 1.3$), 1.40 and 1.02 (CH ₃)
8	4.84 and 3.34 (AA'BB', $J_{AA'} = 4.0, J_{AB} = 5.9, J_{AB'} = 1.7, J_{BB'} = 0.1$), 1.46 (CH ₃)
9	4.73 and 3.29 (AA'BB', J as in 8), 1.46 (CH ₃)
10	4.86 (d, $J = 5.0$), 4.71 (d, $J = 5.0$), 3.37 (t, $J = 5.0$), 3.25 (t, $J = 5.0$), 1.46 (CH ₃)
11	4.93 and 3.59 (AA'BB', $J_{AA'} = 3.0, J_{AB} = 6.9, J_{AB'} = 1.1, J_{BB'} = 1.5$), 1.46 (CH ₃)
12	5.11 and 3.50 (AA'BB', $J_{AA'} = 3.8, J_{AB} = 5.6, J_{AB'} = 1.2, J_{BB'} = 0.1$)
13	5.17 and 3.78 (AA'BB', $J_{AA'} = 2.7, J_{AB} = 6.1, J_{AB'} = 1.1, J_{BB'} = 1.0$)

^{a)} In CDCl₃; δ , J [Hz]. — ^{b)} 70 eV; **4a**: 196 (0.1) [M⁺], 95 (100); **4b_c** and **4b_t**: 250 (0.2) [M⁺], 83 (100); **4c**: 304 (0.8) [M⁺], 83 (100); **5a**: 172 (1.2) [M⁺], 113 (100); **5b_c** and **5b_t**: 226 (3) [M⁺], 167 (100); **5c**: 280 (1.6) [M⁺], 221 (100); **6** and **7** (CI): 225 (100) [MH⁺]; **8**, **9**, **10**, and **11** (CI): 333 (100) [MH⁺]; **12** and **13** (CI): 441 (100) [MH⁺]. — ^{c)} On column 2 (cf. Experimental); **6**: 1.01; **8**: 1.02; **9**: 1.02; **10**: 1.02; **12**: 1.05.

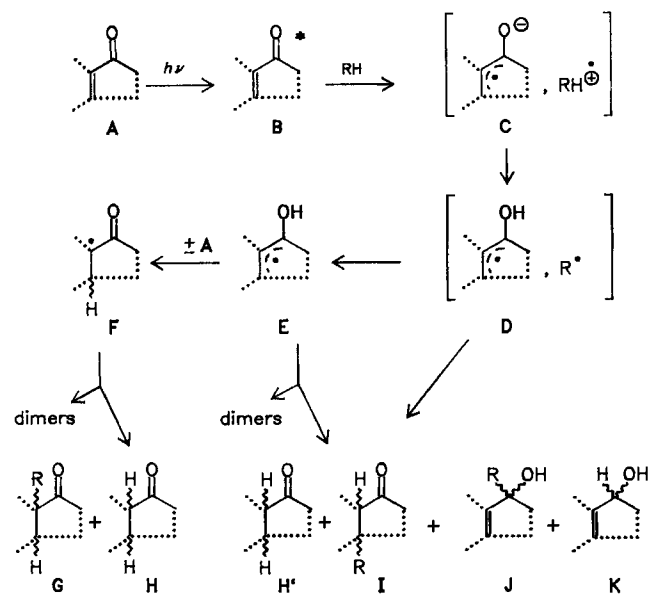
molecular H transfer to¹⁵) and intramolecular H transfer in¹⁶) excited ketones should be discussed as two-step reactions. The first one — electron transfer — represents the photo-reduction step, followed by proton transfer in the radical-cation/radical-anion pair. In intermolecular reactions the effectiveness of this sequence is related to the reduction potential of the ketone, to the oxidation potential of the (donor) solvent, and to the acidity of the radical-cation formed. As we have also gathered experience in electrochemical reductions of 2-cycloalkenones^{17–20}) it seems appropriate to us to provide a sound mechanistic description for the photo-reduction of enones in general.

According to recent reviews on enone photochemistry^{21,22}), photoreduction of enones may take place by either one of two mechanisms: (a) initial H abstraction by the carbonyl oxygen atom and (b) initial H abstraction by the β -olefinic carbon atom. This differential behaviour is ascribed to two distinguishable triplet species, the n,π^* state reacting by path (a) and the π,π^* state by path (b)^{23,24}).

Some other related photochemical reactions of carbonyl compounds have originally been described as so-called *two-*

triplet reactions²⁵), but additional mechanistic evidence usually simplified the picture to the point that the formation of all products became derivable from *one* common triplet intermediate²⁶. In the mechanism given in Scheme 3 all typical enone photoreduction products may be traced back in a convincing manner to one intermediate; the radical E, formed by protonation of the oxygen in the radical-cation/radical-anion pair C — after electron transfer to the excited enone B — and subsequent separation of the cage radical pair D.

Scheme 3



The selective formation of products 5 (corresponding to I) from 1 (corresponding to A) in 2-propanol (RH) thus proceeds by radical coupling on C- β either directly in the radical pair D or between radicals E and R•. The same type of product is also formed from 2-cyclopentenone²⁷. The fact that no allylic alcohols of type K are formed from 1 is due to the stabilization of the unpaired electron at C- β by the vicinal oxygen atom leading to exclusive coupling on this center.

Products of type G have always been observed when A was either a 3-alkyl-, 4,4-dialkyl-, or 3,4,4-trialkyl-2-cyclohexenone. The formation of these products can easily be rationalized in assuming that intermediate E is sterically too hindered at C- β to add either R• or H• and therefore will transfer hydrogen to a second molecule A to give the thermodynamically more stable²⁸ radical F which is then able to couple with R• or H• to afford products G or H, respectively. The saturated ketone formed from E, i.e. H', may be identical with H, or alternatively have different stereochemistry. The formation of pinacols from E or of 1,4-dicarbonyl compounds from F will depend on the relative rates of the other competing processes, which again will depend on the radical R• stemming from the solvent RH. Both types of reactions have been observed, e.g. pinacol formation from

testosterone acetate²⁹ and 1,4-dicarbonyl compound formation from 5,5-dimethyl-2(5H)-furanone³⁰.

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Experimental

General: IR: Perkin-Elmer PE 399. — UV: Perkin-Elmer PE 552. — ¹H- and ¹³C-NMR: Bruker AC 250 or WH 400 in CDCl₃ with TMS as internal standard. — MS: Varian MAT 311A, 70 eV. — Photolyses were run in 0.1 M degassed (Ar) solutions in a Rayonet RPR-100 photoreactor using 350 nm lamps. The photoreactions were monitored by analytical GC on a 25-m glass capillary coated with SE 30. — Enantioselective GC-analyses³¹ were performed on a glass capillary coated with either heptakis(3-*O*-butyryl-2,6-di-*O*-pentyl)- β -cyclodextrin (column 1) or octakis(3-*O*-butyryl-2,6-di-*O*-pentyl)- γ -cyclodextrin (column 2). — Silica gel 60, 70–230 mesh (Merck) was used as stationary phase for column chromatography with C₆H₆/EtOAc (9:1) as eluent, unless otherwise stated.

Starting Materials: 2,2-Dimethyl-3(2H)-furanone⁶ (1a), trifluoroacetone cyanohydrin¹², and hexafluoroacetone cyanohydrin³² were synthesized according to the references indicated.

2-Methyl-2-trifluoromethyl-3(2H)-furanone (1b) was prepared from 3-hydroxy-3-trifluoromethyl-2-butanone¹² (2b) and ethyl formate in analogy to 1a according to ref.⁶ in 31% yield, b.p. 64°C/20 Torr. — IR (CCl₄): $\tilde{\nu}$ = 1724. — UV (C₆H₁₂): λ_{\max} (lg ϵ) = 321 (1.700), 251 (3.849). — ¹H NMR: δ = 8.30 and 5.77 (AB, *J* = 2.6), 1.65 (s, 3H). — ¹³C NMR: δ = 197.9 (s), 177.7 (d), 121.7 (q, *J*_{CF} = 283), 106.0 (d), 83.7 (q, *J*_{CF} = 38), 16.1 (q). — MS: *m/z* (%) = 166 (71) [M⁺], 54 (100). — Enantioselective GC: α (column 1) = 1.22.

C₆H₅F₃O₂ (166.1) Calcd. C 43.39 H 3.03
Found C 43.47 H 3.12

cis- and trans-4,5-Dihydro-5-hydroxy-2-methyl-2-trifluoromethyl-3(2H)-furanone (3b_c and 3b_t) were prepared as a 1:9 mixture (according to ¹H-NMR) in analogy to 3a according to ref.⁶ in 35% yield, b.p. 56–60°C/0.2 Torr, contaminated with 10% of 1b. — ¹H NMR: minor component (3b_c): δ = 5.90 (d, *J* = 6.0), 2.94 (dd, *J* = 6.0, 19.2), 2.67 (d, *J* = 19.2), 1.44 (s, 3H); major component (3b_t): δ = 5.94 (d, *J* = 5.8), 2.91 (dd, *J* = 5.8, 18.2), 2.62 (d, *J* = 18.2), 1.44 (s, 3H). — ¹³C NMR: δ = 206.8 (s), 122.8 (q, *J*_{CF} = 283), 95.0 (s), 80.5 (q, *J*_{CF} = 38), 43.4 (t, major component), 42.7 (t, minor component), 18.3 (q).

3-Hydroxy-4,4,4-trifluoro-3-trifluoromethyl-2-butanone (2c) was prepared from hexafluoroacetone cyanohydrin in analogy to 2b according to ref.¹² in 79% yield, b.p. 90°C/760 Torr. — ¹H NMR: δ = 5.00 (OH), 2.60 (s, 3H). — ¹³C NMR: δ = 194.9 (s), 120.6 (q, *J*_{CF} = 283), 80.0 (sept, *J*_{CF} = 38), 25.6 (q).

C₅H₄F₆O₂ (210.1) Calcd. C 28.59 H 1.92
Found C 28.65 H 2.01

2,2-Bis(trifluoromethyl)-3(2H)-furanone (1c) was prepared from 2c in analogy to 1b in 14% yield, b.p. 95°C/80 Torr. — IR (CCl₄): $\tilde{\nu}$ = 1746. — UV (C₆H₁₂): λ_{\max} (lg ϵ) = 322 (1.481), 250 (3.692). — ¹H NMR: δ = 8.46 and 5.94 (AB, *J* = 2.6). — ¹³C NMR: δ = 189.1 (s), 179.4 (d), 119.9 (q, *J*_{CF} = 283), 85 (sept, *J*_{CF} = 38). — MS: *m/z* (%) = 220 (7) [M⁺], 69 (100).

C₆H₂F₆O₂ (220.1) Calcd. C 32.75 H 0.92
Found C 33.01 H 1.00

Photolyses of 1

a) *In the Presence of 2,3-Dimethyl-2-butene*: Solutions containing $2 \cdot 10^{-3}$ mol of **1** and 1.68 g ($2 \cdot 10^{-2}$ mol) of alkene in 20 ml of C_6H_6 were irradiated for 14 h. Evaporation of the solvent and bulb-to-bulb distillation (80°C/0.1 Torr) afforded 208 mg (53%) of 3,3,6,6,7,7-hexamethyl-2-oxabicyclo[3.2.0]heptan-4-one⁷⁾ (**4a**), 360 mg (72%) of a 2:3 mixture of **4b_i** and **4b_o** [chromatography of diastereomers **4b** giving 45 mg (9%) of (1 α ,3 β ,5 α)-3,6,6,7,7-pentamethyl-3-trifluoromethyl-2-oxabicyclo[3.2.0]heptan-4-one (**4b_i**) and 60 mg (12%) of (1 α ,3 α ,5 α)-3,6,6,7,7-pentamethyl-3-trifluoromethyl-2-oxabicyclo[3.2.0]heptan-4-one (**4b_o**)], and 432 mg (71%) of 6,6,7,7-tetramethyl-3,3-bis(trifluoromethyl)-2-oxabicyclo[3.2.0]heptan-4-one (**4c**), all colourless liquids.

4b: $C_{12}H_{17}F_3O_2$ (250.3) Calcd. C 57.60 H 6.85
Found C 57.35 H 6.93

4c: $C_{12}H_{14}F_6O_2$ (304.3) Calcd. C 47.38 H 4.64
Found C 47.61 H 4.71

b) *In 2-Propanol*: Solutions of $2 \cdot 10^{-3}$ mol of **1** in 2-propanol were irradiated for 18 h. Workup as above afforded 228 mg (66%) of 4,5-dihydro-5-(1-hydroxy-1-methylethyl)-2,2-dimethyl-3(2H)-furanone (**5a**), 307 mg (68%) of a 1:1 mixture of **5b_i** and **5b_o** [chromatography afforded at best 4:1 mixtures of *cis*- and *trans*-4,5-dihydro-5-(1-hydroxy-1-methylethyl)-2-methyl-2-trifluoromethyl-3(2H)-furanone contaminated with the other diastereoisomer], and 375 mg (67%) of 4,5-dihydro-5-(1-hydroxy-1-methylethyl)-2,2-bis(trifluoromethyl)-3(2H)-furanone (**5c**), all colourless liquids.

5a: $C_9H_{16}O_3$ (172.3) Calcd. C 62.77 H 9.36
Found C 62.33 H 9.47

5b: $C_9H_{13}F_3O_3$ (226.2) Calcd. C 47.80 H 5.79
Found C 48.13 H 5.92

5c: $C_9H_{10}F_6O_3$ (280.2) Calcd. C 38.59 H 3.60
Found C 38.92 H 3.75

c) *Photodimerization*: Solutions containing $2 \cdot 10^{-3}$ mol of **1** in 20 ml of C_6H_6 (**B**) or CH_3CN (**A**) were irradiated for 40 h, and the solvent (and unreacted **1**) was evaporated. The crude yields of tricyclic dimers were from **1a**: 55% (**B**), 59% (**A**); from **1b**: 81% (**B**), 61% (**A**); from **1c**: 49% (**B**), 37% (**A**). From the mixture of **6** and **7**, (1 α ,2 β ,6 β ,7 α)-4,4,9,9-tetramethyl-3,10-dioxatricyclo[5.3.0.0^{2,6}]decan-5,8-dione (**6**) is obtained by recrystallization from pentane⁷⁾. Chromatography of the mixture **8**–**11** afforded two fractions; the first one consisted of 78% of **8**, 8% of **9**, and 14% of **11**, from which (1 α ,2 β ,4 β ,6 β ,7 α ,9 α)-4,9-dimethyl-4,9-bis(trifluoromethyl)-3,10-dioxatricyclo[5.3.0.0^{2,6}]decan-5,8-dione (**8**), m.p. 159°C, was obtained by recrystallization from pentane; the second one consisted of 82% of **10** and 18% of an unknown photodimer, from which (1 α ,2 β ,4 α ,6 β ,7 α ,9 α)-4,9-dimethyl-4,9-bis(trifluoromethyl)-3,10-dioxatricyclo[5.3.0.0^{2,6}]decan-5,8-dione (**10**), m.p. 97 to 99°C, was obtained by recrystallization from pentane. From the mixture of **12** and **13**, (1 α ,2 β ,6 β ,7 α)-4,4,9,9-tetrakis(trifluoromethyl)-3,10-dioxatricyclo[5.3.0.0^{2,6}]decan-5,8-dione (**12**) was obtained by chromatography as a colourless oil.

8: $C_{12}H_{10}F_6O_4$ (332.2) Calcd. C 43.39 H 3.03
Found C 43.56 H 3.10

12: $C_{12}H_4F_{12}O_4$ (440.2) Calcd. C 32.75 H 0.92
Found C 33.01 H 1.05

Comparative Relative Rate Measurements: Photolyses of 1-ml solutions of **1** (concentrations as above) were run in a merry-go-round setup. The formation of photoproducts was monitored every 10 min by GC using tetradecane as internal standard. Average values of three runs (error $\pm 10\%$) are given (see Results).

CAS Registry Numbers

1a: 35298-48-7 / **1b**: 123902-69-2 / **1c**: 123902-70-5 / **2b**: 661-78-9 / **2c**: 15237-52-2 / (*cis*)-**3b**: 123902-82-9 / (*trans*)-**3b**: 123902-83-0 / **4a**: 82555-04-2 / **4b_i**: 123902-71-6 / **4b_o**: 124018-48-0 / **4c**: 123902-72-7 / **5a**: 123902-73-8 / **5b_i**: 123902-74-9 / **5b_o**: 123902-75-0 / **5c**: 123902-76-1 / **6**: 42833-05-6 / **7**: 123902-77-2 / **8**: 123902-78-3 / **9**: 124018-49-1 / **10**: 124018-50-4 / **11**: 123902-79-4 / **12**: 123902-80-7 / **13**: 123902-81-8 / Me_2CHOH : 67-63-0 / $(Me_2C)_2$: 563-79-1

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