85. Photochemistry of 6,6-Dimethyl- and 2,2,6,6-Tetramethyl-2*H*,6*H*-pyran-3-one

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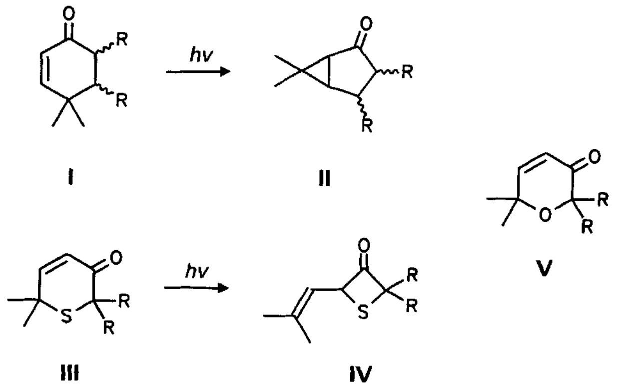
The title compounds **1a** and **1b** have been synthesized in two steps from the saturated pyran-3-ones **2a** and **2b**, respectively. Upon irradiation (254 nm or 350 nm) in dilute solutions (10^{-3}–10^{-2} M), compounds **1** undergo a formal [4 + 2] cycloreversion from the excited triplet state to give (2-methylprop-1-enyl)ketene (**11**) and either formaldehyde or acetone, ketene **11** being trapped by H_2O or MeOH to afford 4-methylpent-3-enoic acid (**5**) or its methyl ester **4** in 75–85% isolated yield. In this (monomolecular) photoreaction, heterocycles **1** differ from their alicyclic counterparts, *i.e.*, 4,4-dimethylcyclohex-2-enone (**10a**) and 4,4,6,6-tetramethylcyclohex-2-enone (**10b**), as *no* rearrangement to a 4-oxabicyclo[3.1.0]hexan-2-one occurs. On the other hand, the photochemical behavior of pyranone **1a** in bimolecular reactions (cyclodimerization, [2 + 2] cycloaddition to 2,3-dimethylbut-2-ene) resembles that of enone **10a**.

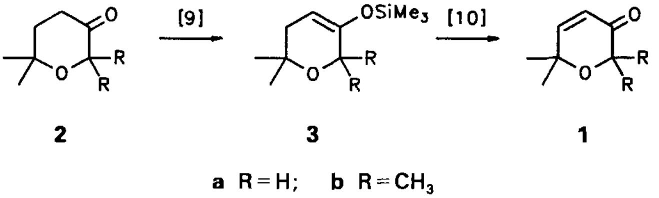
Introduction. – The photoisomerization of 4,4-dialkylcyclohex-2-enones **I** to 6,6-dialkylbicyclo[3.1.0]hexan-2-ones **II** proceeds usually to the exclusion of competing processes albeit with low quantum efficiencies [1–3]. To better understand the mechanism of this so-called *lumiketone* rearrangement, *i.e.*, the C(3)–C(5) bond-formation and the C(5)–C(4) bond-cleavage steps, we had developed two lines of approach. The first one [4] consisted in looking for the stereochemical outcome of this rearrangement for 4,4-dimethylcyclohex-2-enones with an additional alkyl or F substituent on C(5) or C(6). The second one consisted in replacing C(5) by a heteroatom. We have recently reported results on the photoisomerization of 2*H*,6*H*-thiin-3-ones **III** to 2-(alk-1-enyl)thietan-3-ones **IV** [5]. Here, we report on the synthesis and the photochemistry of the corresponding oxacycles **V** (*Scheme 1*).

Scheme 1



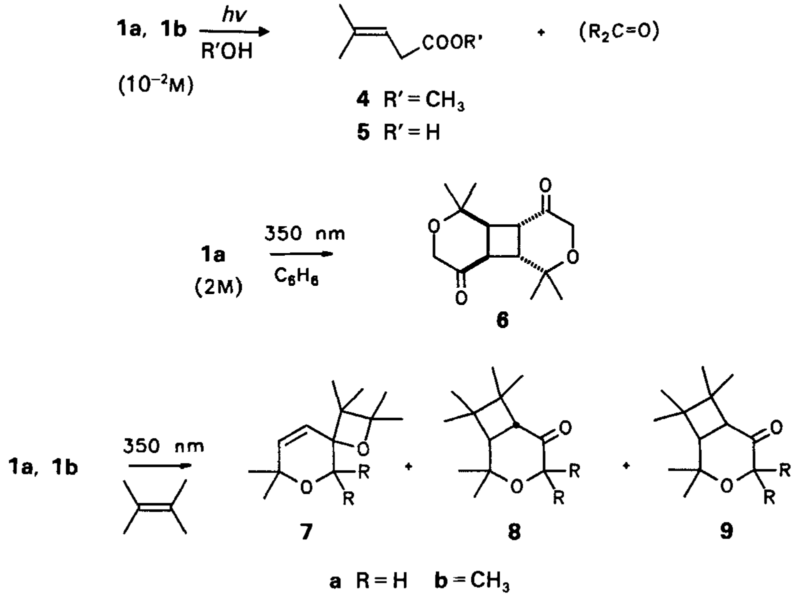
Results. – There are only very few reports in the literature on the synthesis of 2*H*,6*H*-pyran-3-ones. The parent (unsubstituted) compound has been synthesized from 1,1-diethoxyethanol and 3-bromopropyne [6], but this sequence does not easily allow the synthesis of compounds like **1a** or **1b**, *i.e.*, with geminal dimethyl groups on C(6). On the other hand, both tetrahydropyran-3-ones **2a** [7] and **2b** [8] are known compounds. Among the various methods for converting a cyclic ketone into the α,β-unsaturated carbonyl compound, we used the sequence **2**→trimethylsilyl enol ether **3** (according to [9])→**1** (*Scheme 2*) using equimolar amounts of Pd^{II} for the dehydrogenation step [10].

Scheme 2



GC Monitoring of irradiations of **1a** or **1b** (350 nm or 254 nm, 10^{-3}–10^{-2} M, MeCN, C_6H_6, *t*-BuOH) turned out to be disappointing, as it only indicated loss of starting material without formation of any new product; however, a (serendipitous) experiment in MeOH indicated almost quantitative conversion of both compounds to one new common product, which was recognized as being methyl 4-methylpent-3-enoate (**4**; *Scheme 3*). Indeed, monitoring the reaction by ^{1}H-NMR in CD_3OD indicates the formation of tetradeuterated **4** as well as of bis(trideuteromethoxymethane) from **1a** and acetone from

Scheme 3



1b. The corresponding acid **5** is formed in again almost quantative yield from both oxacycles in MeCN or *t*-BuOH containing 1–2% H_2O, besides 1,3,5-trioxane from **1a** and acetone from **1b**, as monitored by ^{1}H-NMR (acid **5** is not detected by GC due to decarboxylation). An additional product **6** is formed from **1a** upon irradiation at higher concentration. Best yields of **6** are obtained on irradiation (350 nm) of a 2M solution of **1a** in C_6H_6, as product **6** is almost insoluble in this solvent. No corresponding reaction is observed for **1b**. From spectral analysis, compound **6** turns out to be the HT-cyclodimer with *cis-anti-cis*-configuration. Irradiation (350 nm) of **1a** in the presence of a tenfold excess of 2,3-dimethylbut-2-ene affords a 2:3:1 mixture of oxetane **8a** and *trans*- and *cis*-fused oxabicyclooctanones **8a** and **9a**, while **1b** affords only oxetane **7b** and some acid **5** under these conditions, as monitored by ^{1}H-NMR and GC (*Scheme 3*).

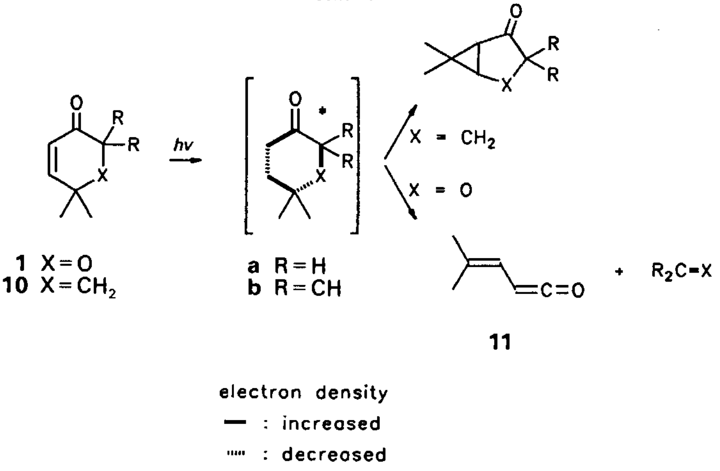
Comparative irradiations of **1a** in various solvents and at both wavelengths (350 and 254 nm) indicate that the quantum yield for disappearance of starting material is independent of these parameters ($\Phi_{-1a} = 0.015$ in MeCN containing 1% H_2O at 350 nm), the conversion of excited **1a** to **5** occurring about twice as fast as that of excited **1b**. Quenching of excited **1a** and **1b** by naphthalene suggests a reactive triplet excited state (*Table*).

Table. *Quantum Yields* (350 nm) *and Relative Rates* (254 nm) *for Disappearance of Starting Material* (*Solvent*)

	1a	**1b**	**10a**	**10b**
MeCN/350 nm	0.015	0.006	0.014 [4]	0.017 [4]
C_6H_6/350 nm	0.015	0.009	0.001	
MeOH/350 nm	0.016	0.009	0.039	
t-BuOH/254 nm	*1*	*0.4*	*0.9*	

Discussion. – The differential outcome in the light-induced monomolecular reactions (the behavior in bimolecular reactions being alike) of pyran-3-ones **1** and their carbocyclic counterparts, *i.e.*, 4,4-dimethylcyclohex-2-enone (**10a**) and 4,4,6,6-tetramethylcyclohex-2-enone (**10b**), is outlined in *Scheme 4*, assuming a (qualitative) electron distribution for the excited enones as indicated. While compounds **10** undergo isomerization

Scheme 4



with a pronounced solvent dependency regarding the quantum yields (tenfold higher efficiency in either MeCN or *t*-BuOH comparing to benzene or cyclohexane), pyranones **1** undergo exclusive cycloreversion to a carbonyl compound (formaldehyde or acetone) and ketene **11** with very similar rates in both polar and apolar solvents.

This discrepance in behavior between **1** and **10** is most probably mainly due to the difference in bond energies between a C=C and a C=O bond (the energy of the latter is *ca.* 150 kJ/mol higher). This is already reflected in the mass spectra of these compounds which all exhibit a common base peak (*m/z* 96) corresponding to the radical ion of **11**, but the relative intensities of the peaks corresponding to the molecular ions of compounds **10** (40% for **10a**, 3% for **10b**) are higher than those for compounds **1** (19% for **1a**, < 0.01% for **1b**).

The fact that no oxabicyclohexanones are formed from **1** might additionally be due to that S_H2-reactions on ether-O-atoms are even less favorable than the corresponding substitutions on the C-atom. Dialkyl peroxides are known to react with alkyl radicals to afford an ether and an alkoxy radical, but alkyl group exchange for ethers *via* a radical mechanism – a well known reaction for sulfanes – seems to be unknown [11].

Experimental Part

General. Photolyses: *Rayonet-RPR-100* photoreactor equipped with either 350-nm (*A*) or 254-nm (*B*) lamps and a merry-go-round setup. GC: 30-m *SE 30* capillary column. UV Spectra: in nm (log ε). IR Spectra: in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: at 400 and 100.63 MHz, resp.; chemical shifts in ppm rel. to TMS (= 0 ppm), coupling constants *J* in Hz. MS: at 70 eV; in *m/z* (rel. intensity in %).

3-(Trimethylsilyloxy)pyrans **3**. Prepared from dihydropyranones (**2a** [7], **2b** [8]), Me_3SiCl, NaI, and Et_3N according to [9]. *5,6-Dihydro-6,6-dimethyl-3-(trimethylsilyloxy)-2*H*-pyran* (**3a**): 85%, b.p. 78–82°/17 Torr. *5,6-Dihydro-2,2,6,6-tetramethyl-3-(trimethylsilyloxy)-2*H*-pyran* (**3b**): 87%, b.p. 81°/15 Torr.

Pyranones **1**. Prepared from **3** and stoichiometric amounts of $Pd(OAc)_2$ in MeCN according to [10].

*6,6-Dimethyl-2*H*,6*H*-pyran-3-one* (**1a**): 86%. B.p. 70°/18 Torr. UV (MeCN): 341 (1.47), 223 (4.01). IR (neat): 1692. ^1H-NMR ($CDCl_3$): 6.79 (*d*, *J* = 10.7); 5.85 (*d*, *J* = 10.7); 4.07 (*s*, 2 H); 1.29 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 194.6 (*s*); 156.3 (*d*); 124.3 (*d*); 72.3 (*s*); 67.3 (*t*); 25.6 (*q*). MS: 126 (19, M^+), *96*.

*2,2,6,6-Tetramethyl-2*H*,6*H*-pyran-3-one* (**1b**): 70%. B.p. 69–71°/15 Torr. UV (MeCN): 341 (1.71), 215 (3.98). IR (neat): 1688. ^1H-NMR ($CDCl_3$): 6.83 (*d*, *J* = 10.7); 5.91 (*d*, *J* = 10.7); 1.43 (*s*, 6 H); 1.39 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 198.5 (*s*); 154.2 (*d*); 121.1 (*d*); 77.4 (*s*); 71.1 (*s*); 29.2 (*q*); 26.6 (*q*). MS: 154 (0.01, M^+), *96*.

Methyl 4-Methylpent-3-enoate (**4**). A soln. of $5 \cdot 10^{-3}$ mol of **1a** or **1b** in 500 ml of MeOH is irradiated (lamps *A*) for 72 h (monitoring by GC). The soln. is the diluted with 1000 ml of H_2O and extracted with pentane (3 × 30 ml). After drying the pentane soln. ($MgSO_4$), the solvent is distilled off through a *Vigreux* column. Distillation then affords 450–500 mg (70–80%) of **4**. B.p. 145–148°/660 Torr.

4-Methylpent-3-enoic Acid (**5**). A soln. of $5 \cdot 10^{-3}$ mol of **1a** or **1b** in 490 ml of *t*-BuOH and 10 ml of H_2O is irradiated (lamps *B*) in a quartz vessel for 6 h. After removal of the solvent (rot. evap.), the residue is purified by bulb-to-bulb distillation at 95°/10 Torr to afford 450–500 mg (80–90%) of **5**.

cis-transoid-cis-*3,3,9,9-Tetramethyl-4,10-dioxatricyclo[6.4.0.0^{2,7}]dodecane-6,12-dione* (**6**). A soln. of 252 mg ($2 \cdot 10^{-3}$ mol) of **1a** in 1 ml of C_6H_6 is irradiated (lamps *A*) for 96 h. The white precipitate is filtered off and recrystallized from $CHCl_3$/hexane to afford 204 mg (81%) of **6**. M.p. 190°. ^1H-NMR ($CDCl_3$): 4.21, 4.17 (*AB*, *J* = 19.5, 4 H); 3.43, 2.47 (*AA'XX'*, $J_{AB} = 10.7$, $J_{AB'} = 4.7$, 4 H); 1.28 (*s*, 6 H); 1.23 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 210.6 (*s*); 72.1 (*s*); 68.8 (*t*); 43.3 (*d*); 42.8 (*d*); 24.8 (*q*); 22.5 (*q*). MS: 252 (1, M^+), 43.

Photocycloaddition of **1** *to 2,3-dimethlybut-2-ene.* A soln. of 10^{-4} mol of **1a** or **1b** and 168 mg ($2 \cdot 10^{-3}$ mol) of 2,3-dimethlybut-2-ene in 1 ml of C_6D_6 is irradiated (lamps *A*) for 72 h. Monitoring the reaction by ^1H-NMR indicates the formation of **7a**, **8a**, and **9a** in a ratio of 2:3:1 from **1a** and of **7b** (exclusively, besides **4**) from **1b**.

2,2,3,3,7,7-Hexamethyl-1,6-dioxaspirot[3.5]non-8-ene (**7a**): ^{1}H-NMR ($CDCl_3$): 5.93 (*dd*, $J = 10.7, 1.5$); 5.67 (*d*, $J = 10.7$); 4.10 (*dd*, $J = 11.7, 1.5$); 3.68 (*d*, $J = 11.7$).

6α,7β-2,2,7,7,8,8-Hexamethyl-3-oxabicyclo[4.2.0]octan-5-one (**8a**): ^{1}H-NMR ($CDCl_3$): 3.98, 3.78 (*AB*, $J = 17.1$, 2 H); 2.71 (*d*, $J = 14.9$); 2.22 (*d*, $J = 14.9$).

6α,7α-2,2,7,7,8,8-Hexamethyl-3-oxabicyclo[4.2.0]octan-5-one (**9a**): ^{1}H-NMR ($CDCl_3$): 4.02, 3.65 (*AB*, $J = 14.8$, 2 H); 2.52 (*d*, $J = 9.2$); 2.26 (*d*, $J = 9.2$).

2,2,3,3,5,5,7-Octamethyl-1,6-dioxaspiro[3.5]non-8-ene (**7b**): ^{1}H-NMR ($CDCl_3$): 6.04 (*d*, $J = 10.4$); 5.63 (*d*, $J = 10.4$).

Comparative Photolyses of **1** *and* **10** *in Different Solvents* (Merry-go-round experiments). Equimolar solns. of **1** and **10** were irradiated under conditions of total light absorption using a merry-go-round setup. The degree of conversion was monitored by GC using undecane as internal standard.

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