Photochemical Synthesis of 4-Oxobutanal Acetals and of 2-Hydroxycyclobutanone Ketals

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Received October 12, 1998

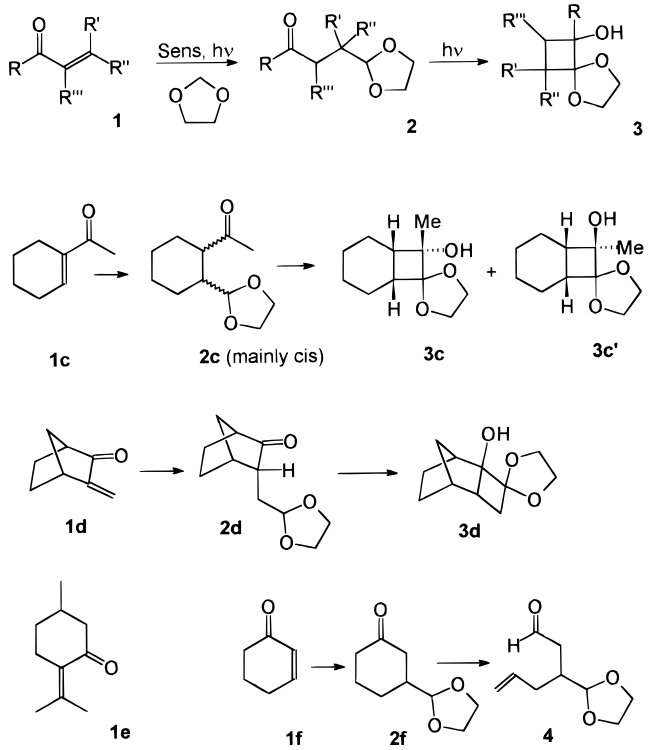
Irradiation of α,β-unsaturated ketones (aliphatic, both open chain and cyclic as well as aryl substituted) in 1,3-dioxolane in the presence of a sensitizer (benzophenone or anthraquinone) led to 4-oxobutanal acetals in fair to excellent yield through a very simple procedure (workup in most cases by bulb-to-bulb distillation). The resulting acetals were irradiated to give 2-hydroxycyclobutanone ketals, again through a simple procedure that gave a good yield with open-chain aliphatic derivatives.

2-Hydroxycylobutanones and their ketals are known for the smooth acid-catalyzed ring contraction to cyclopropanecarboxyaldehydes[1] and have been shown to be versatile intermediates in organic synthesis.[2] Access to these compounds is limited, however. The usual preparation involves the acyloin condensation of succinic ester derivatives,[3] a method of obviously limited scope, and to our knowledge the only other reported synthesis starts from cyclobutanone through photosensitized oxidation of the corresponding silyl enol ether.[4] It thus appeared worthwhile to look for a more flexible procedure. We thought that a versatile method for the four-membered ring would be based on a 3 + 1 path, precisely a double-radical addition to an unsaturated carbonyl. In this paper, we report a two-step photochemical procedure leading to spiro 2-hydroxycyclobutanone ketals via 4-oxobutanal acetals and comment on the scope of the reactions involved.

Results

Our approach for forming the four-membered ring via a 3 + 1 scheme was based upon two sequential radical additions. Hydrogen abstraction by triplet state ketones is a convenient procedure for activation of a C−H bond. Thus, an obvious reagent was a formaldehyde acetal, and we chose commercially available 1,3-dioxolane. The first step we planned was addition to an α,β-unsaturated ketone through a photosensitized reaction. The resulting 1,4-dicarbonyl monoacetal had an activated γ hydrogen, and thus, intramolecular reaction was expected to be efficient. It was hoped that the biradical would then undergo Yang cyclization[5] to give the target cyclobutanol rather than undergo fragmentation.

Scheme 1



Open-Chain Enones. Irradiation (2 h) of methyl vinyl ketone (**1a**) in dioxolane in the presence of benzophenone as the sensitizer gave 4-oxobutanal ethylenacetal (**2a**) as the only GC-detected product. This was isolated in a 40% yield by bulb-to-bulb distillation, the low yield being due to the loss by evaporation during the workup (Scheme 1, Table 1). The residue was a mixture of benzophenone and benzopinacol. The distilled acetal was dissolved in MeCN and irradiated by a low-pressure mercury arc. To our delight, this procedure gave the desired spiro acetal **3a** as the only volatile product. A simple workup such as bulb-to-bulb distillation or silica gel chromatography gave the product in 40% isolated yield (again limited by evaporation).

With the somewhat higher boiling mesityl oxide (**1b**), the reaction occurred analogously and the isolated yield

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10.1021/jo982053t CCC: $18.00
Published on Web 06/11/1999

Table 1. Photochemical Synthesis of 4-Oxobutanal Acetals (2) and of 2-Hydroxycyclobutanone Ketals (3)

substrate[a]	R	R′	R″	sensitizer	t_{IR} (h)	product **2** (% yield)	t_{IR} (h)	product **3** or other (% yield)
1a	Me	H	H	Ph_2CO, 0.02 M	2	**2a** (40)	16 h	**3a** (40)
1b	Me	Me	Me	Ph_2CO, 0.02 M	5	**2b** (55)	20 h	**3b** (58)
1c	Me	H	*b*	Ph_2CO, 0.02 M	3	**2c** (92)	20 h	**3c** + **3c′** (65)
1d	*c*			AQ,[d] 0.002 M	30	**2d** (80)	10 h	**3d** (25)[e]
1e	*f*			Ph_2CO, 0.02 M	5	*g*		
1f	$-(CH_2)_4-$		H	Ph_2CO, 0.02 M	8	**2f** (80)	7 h	**4** (25)
1g	$-(CH_2)_5-$		H	Ph_2CO, 0.02 M	5	**2g** (55)	10 h	*h*
1h	*i*			Ph_2CO, 0.005 M	20	**2h** (45)	12 h	**3h** (10)[e]
1i	Ph	H	H	AQ,[d] 0.002 M	3	**2i** (65)	12 h	**5** (50)
1j	Me	H	Ph	AQ,[d] 0.002 M	12	**2j** (35)	12 h	*g*
1k	Ph	H	Ph	AQ,[d] 0.002 M	60	**2k** (85)	6 h	**5** (50), **6** (44)

[a] 0.05 M, R‴ = H unless otherwise indicated. [b] R″−R‴ = $-(CH_2)_4-$. [c] 3-Methylene-2-norbornanone. [d] AQ = 9,10-anthraquinone. [e] Product detected by GC/MS but not isolated. [f] Pulegone. [g] No reaction. [h] The substrate reacts, but no product has been isolated. [i] Phorone (2,6-dimethyl-buta-2,5-dien-4-one).

both of the open chain acetal **2b** and of the hydroxycyclobutane **3b** increased considerably with the same simple workup.

Cyclic Enones. The effect of the constraint imposed by a cyclic structure was then examined. Thus, 1-acetylcyclohexene (**1c**) gave the saturated monoacetal (**2c**) in excellent yield with the cis isomer predominating (7:1). In turn, this was efficiently cyclized by further irradiation to give the two diastereoisomeric tricyclic alcohols (**3c** + **3c′**, ratio 2:1) in a fair yield. In the case of 3-methylene-2-norbornanone (**2d**), anthraquinone (AQ) was used as sensitizer in the place of benzophenone, since the latter was unsatisfactorily separated from the photoproduct by bulb-to-bulb distillation. Under these conditions, the reaction was slower but gave a good yield of adduct **2d**. This in turn underwent photocyclization to **3d**, though in a poor yield. On the other hand, practically no reaction was obtained by sensitized irradiation of pulegone (**1e**) in dioxolane.

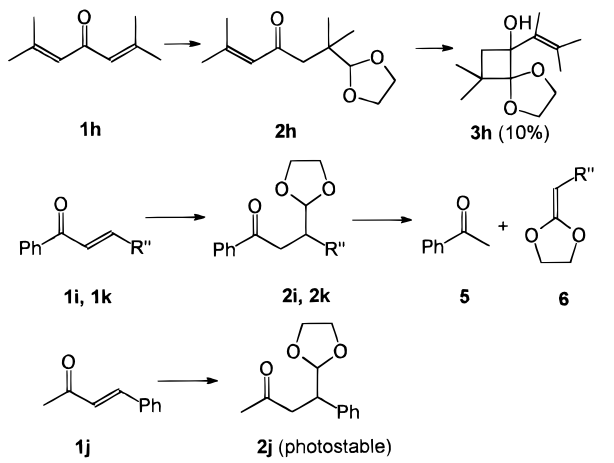
2-Cyclohexen-1-one (**1f**) was conveniently alkylated to **2f** through the same method. However, further irradiation of the latter derivative mainly gave the open chain aldehyde **4** rather than a fused cyclobutane. As for 2-cyclohepten-1-one (**1g**), alkylation to **2g** was again successful, but photolysis of the latter led to no isolated product.

Cross-Conjugated and Aryl Ketones. The effect of conjugation was next explored. Starting from phorone (**1h**), monoalkylated **2h** was obtained in a reasonable yield in the presence of a lower than usual benzophenone concentration (0.005 M) and in a slow reaction (Scheme 2, Table 1). Ketone **2h** reacted photochemically, and cyclized **3h** was formed, as shown by GC/MS, though in too low an amount to allow isolation.

Three aryl derivatives were tested (**1i**−**k**). In every case, alkylation in dioxolane was successful, provided that anthraquinone rather than benzophenone was used as the sensitizer. Among the saturated ketones thus obtained, the two 1-phenyl ketones **2i** and **2k** underwent photochemical fragmentation to give acetophenone (**5**) and a ketene acetal (**6**, isolated from **2k**), whereas the 3-phenyl ketone **2j** was recovered unchanged after several hours of irradiation.

Phosphorescence of Ketones 2. The phophorescence of the alkyl ketones **2** was measured in EPA glass at 77 K. Ketones **2a**−**d** exhibited a strongly vibrationalized emission between 410 and 550 nm ($\Delta\nu$ ca. 1600 cm^{-1}), as is typical of aliphatic ketones. The vinyl (**2h**) or aryl ketones (**2i**, **2k**) again showed a well-resolved phosphorescence spectrum, which was practically superimposable to that of mesityl oxide and to that of acetophenone, respectively. The 2-phenylethyl ketone **2j**, on the other hand, showed a poorly structured emission centered at 440 nm.

Scheme 2



Discussion

Scope of the Method. Photosensitized Masked Formylation of α-Enones. Conjugate alkylation via photochemically generated radicals is an appealing, yet not extensively employed, synthetic method.[6] Excited α-enones are poor hydrogen abstractors, and direct irradiation is an inefficient procedure for generating radicals. However, sensitized irradiation is efficient, and both Fraser-Reid and Bundy reported the successful alkylation of some cyclic α,*β*-unsaturated ketones by alcohols and other H donors upon irradiation in the presence of benzophenone.[7] Similar results have been obtained by Inomata with α,*β*-unsaturated sulfones.[8] A subsequent mechanistic study by Fraser-Reid, Mariano, and Beckwith[9] showed that benzophenone acts as a chemical sensitizer, i.e., abstracts hydrogen from the substrate generating the desired alkyl radical and the stabilized diphenyl ketyl radical. The latter species in

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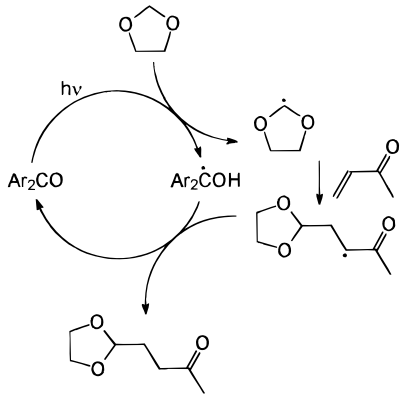
Scheme 3



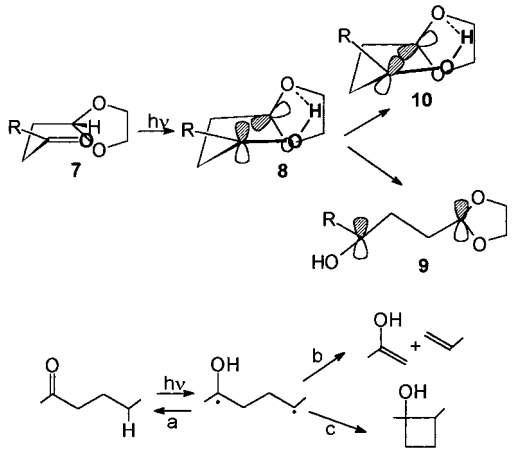
part dimerizes to the pinacol and in part gives back benzophenone though hydrogen transfer to the adduct radical.

The present reaction follows the same mechanism (Scheme 3). The sensitizer is required for the process to occur and is partially reduced during the course of the reaction, which stops when it is consumed. However, while previous works used 1 equiv or excess benzophenone,[8,9] we find that the present reactions conveniently proceed by using a 40% amount of this sensitizer with respect to the substrate. In the case of phorone, the best chemical yield is indeed obtained with a 10% addition of benzophenone, although this requires a somewhat longer irradiation time. This shows that in fact a large part of the sensitizer is recovered via H-donation from the ketyl radical through a chemical sensitization cycle (Scheme 3). From the preparative point of view, using a reduced amount of sensitizer is an advantage, since it simplifies the workup procedure.

With aliphatic α-enones, benzophenone is consistently a good choice; xanthone, for instance, gives a lower yield. With aryl ketones, however, anthraquinone turns out to be a better sensitizer. This is undoubtedly because of the more intense and red-shifted absorption ($\epsilon_{330} = 3600$ with the spectrum extending up to 420 nm) of AQ with respect to Ph_2CO ($\epsilon_{330} = 150$), a characteristic that becomes determining when the absorption by the substrate itself is stronger. Triplet AQ, though lower in energy, is a nπ* state and abstracts hydrogen as efficiently as Ph_2CO.[10] The advantage of a higher ϵ is partially offset by the poor solubility of AQ (we used it at 2×10^{-3}M concentration), but the reaction, though slower in particularly with strongly absorbing substrates such as chalcone (**1k**), occurs with a good chemical yield and with the additional bonus that the low amount of the sensitizer further simplifies the workup.

With this caution, the photosensitized addition of dioxolane to α-enones becomes a quite general method for the introduction of a masked formyl group and gives a fair to excellent yield of 4-keto aldehyde monoacetals through a very simple protocol. In practically every case, the adduct is the only GC-detected product, and the variation in the yield essentially depends on the volatility of the compounds formed. The efficiency of the process is undoubtedly due to the stability and nucleophilicity of the intermediate α,α-dioxaalkyl radical. The success

Scheme 4



of the reaction with the large array of substrates tested shows that it is insensitive to phenyl substitution (whether in the 1 or 3 position) as well as to incorporation of the chromophore in a ring and to sterical hindering; e.g., it occurs efficiently with the β,β-disubstituted **1b**, though not with the yet more hindered pulegone **1h**. In the case of norbornanone **1e**, hydrogen addition occurs selectively from the side of the methylene bridge, thus giving a single diastereoisomer (**2e**); one of the diastereoisomers is largely predominant from **1c**.

It should be noted that 4-oxobutanal acetals have been previously prepared through multistep procedures by transition metal catalyzed Grignard reactions[11] or via pentenal acetals by selective oxidation.[12] Thus, this simple and general procedure—based on the well-known, but rarely used chemical photosensitization—is a useful alternative to existing methods.

Yang Cyclization. Ketones **2a**−**j** can be divided in three groups as far as their photochemistry is concerned. Open-chain aliphatic ketones and, with a lower yield, bicyclic **2d** cyclize to the hydroxycyclobutanols, aryl derivatives undergo Norrish Type II cleavage, and cyclic ketones undergo Norrish Type I cleavage.

As is well-known, intramolecular H-abstraction is the dominating process for nπ* ketone triplets having an accessible γ-hydrogen. Apart from back-hydrogen transfer (path a in Scheme 4), the resulting 1,4-diradical undergoes either α,β fragmentation (path b, Norrish Type II cleavage) or ring closure to yield a cyclobutanol (path c, Yang cyclization).[13−15] For the presently considered ketones **2**, the lowest triplet is an nπ* state, as shown by the characteristic vibrationalized phosphorescence. Thus, γ-hydrogen abstraction is favored.

The ensuing partitioning of the diradical between cleavage (usually the main process by >5:1) and ring closure is currently rationalized on the basis of stereo-

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electronic factors.[13−17] In the frame of this model, we suggest that hydrogen bonding between the hydroxyl group and the acetal oxygen atom maintains the diradical in the first formed coiled conformation **8** (see Scheme 4), which is best suited for cyclization (via conformer **10**), hindering collapse to the stretched conformation **9** from which α,*β* cleavage results. This applies also to the case of **2d**, which gives highly strained **3d**, though less satisfactorily.

With the α-phenyl ketones **2i** and **2k** *γ* abstraction is again efficient but leads to Norrish Type II fragmentation, as in the case of parent propiophenone.[14,17] Apparently, α-phenyl substitution both slows down conversion to the bonding conformation **10** by sterical hindering and diminishes the drive toward cyclization by delocalizing the unpaired electron over ring. A different case is that of the *β*-phenyl ketone **2j**, which is much less reactive than the other ketones considered. The phosphorescence spectrum is also different in this case, with little vibrational structure. Since the triplet energy of an aliphatic ketones and the benzene derivatives are similar [e.g., E_T (Me_2CO) = 80, (PhMe) = 83 kcal mol^{-1}] the stability of this ketone is probably due to deactivation via an intramolecular exciplex.

Neither of the previous reactions occur when the ketone function is incorporated in a ring, as in cyclohexanone **2f** and cycloheptanone **2g**. A cyclobutanol has been obtained from 2-propylcyclohexanone,[18] but apparently the side chain in position 3 in **2f** is too far for efficient intramolecular hydrogen transfer, and the main process is α cleavage (Norrish Type I reaction) as is typical of cyclic ketones.[19] The following radical disproportionation mainly leads to 5-hexenal (**4**).

Conclusion. Chemical photosensitization, viz, the generation of alkyl radical by hydrogen abstraction followed by back-hydrogen transfer to the adduct radical (Scheme 3), is a well-known method for carrying out radical additions[9] but has been rarely used. The present data show a straightforward application for the synthesis of 4-oxobutenal acetals based on the nucleophilicity of 2-dioxolanyl radicals. In view of the many synthetic applications of 1,4-dicarbonyls, this general and experimentally simple method is an useful alternative to the existing multistep procedures.[11,12] In the case of aliphatic derivatives, the thus formed acetals are photochemically cyclized to hydroxycyclobutanone ketals, offering a general and versatile access to these potentially useful[1]—yet not easily accessible[2,3]—intermediates. The phenyl ketones rather undergo Norrish Type II fragmentation.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded in chloroform-*d* on a 300 MHz spectrometer, and chemical shifts are reported in ppm downfield from TMS. Elemental analyses were performed using a standard instrument. The α,*β*-unsaturated ketones **1** were commercial products, except for 1-phenyl-2-propen-1-one (**1i**), which was prepared by oxidative decarboxylation of 3-benzoylpropionic acid as reported.[20] 1,3-Dioxolane and acetonitrile were used as received as the reaction solvents. 60HR silica gel (0.04−0.063 mm) was used for chromatography, and cyclohexane and ethyl acetate as the eluants were distilled before use. Phosphorescence spectra were measured by means of a commercial spectrofluorimeter fitted with a rotating phosphoroscope.

2-Hydroxy-1-methylcyclobutanone Ethylene Ketal (3a). A solution of 0.408 g of 3-propen-2-one (**1a**, 0.05 M) and 0.437 g of benzophenone (0.02 M) in 120 mL of 1,3-dioxolane was subdivided in three serum-capped quartz tubes. These were flushed with argon for 5 min and irradiated for 2 h by means of six 15 W phosphor-coated low-pressure mercury lamps (center of emission, 360 nm). The solution was evaporated and the residue bulb-to-bulb distilled (Büchi GKR 50 apparatus, 180 °C, 50 Torr) to give 0.341 (40%) of 4-oxopentenal diethylenacetal (2a).[21] This product was dissolved in 40 mL of acetonitrile in two quartz tubes. These were flushed with argon and irradiated for 10 h by means of two 15 W low-pressure mercury arcs. The solution was evaporated and the residue bulb-to-bulb distilled (130 °C, 30 Torr) to give 0.136 g of the title compound. Chromatography on silica gel eluting with a cyclohexane−ethyl acetate 7:3 mixture gave the same yield: ^1H NMR *δ* 1.32 (d, 3H, *J* = 0.9 Hz), 1.65 (dtq, 1H, *J* = 1, 10, 11 Hz), 1.80 (ddd, 1H, *J* = 4, 8, 11 Hz), 2.0 (m, 2H), 2.3 (br s, 1H), 3.9 (m, 4H); ^{13}C NMR *δ* 20.5, 27.6, 31.1, 64.6, 65.2, 78.5, 111.2; IR 3500 cm^{-1}. Anal. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 57.8; H, 8.2.

Analogously prepared were the following compounds (irradiation time and yield reported in Table 1). The characterization of 2,2-dimethyl-4-oxopentenal ethylenacetal (**2b**)[12,22] and 2-benzylidene-1,3-dioxolane (**6**)[23] was previously reported.

2-Hydroxy-2,4,4-trimethylcyclobutanone ethylenketal (3b): bulb-to-bulb distilled (130 °C, 30 Torr); ^1H NMR *δ* 1.08 (s, 3H), 1.1 (s, 3H), 1.32 (s, 3H), 1.53 (d, 1H, *J* = 12.5 Hz), 1.75 (d, 1H, *J* = 12.5 Hz), 2.7 (br s, 1H), 3.9 (m, 4H); ^{13}C NMR *δ* 22.7, 23.6, 23.9, 38.7, 46.5, 65.1, 65.2 76.2, 111.2; IR 3425 cm^{-1}. Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.6; H, 9.4.

2-Acetylcyclohexancarboxyaldehyde ethylenacetal (2c). Obtained as a cis isomer impure of the trans in the ratio ca. 7:1 by bulb-to-bulb distillation (145 °C, 0.1 Torr): ^1H NMR *δ* (cis) 1.35−1.5 (m, 3H), 1.55−1.65 (m, 3H), 1.85−1.95 (m, 3H), 2.12 (s, 3H), 2.82 (dt, 1H, *J* = 5, 6 Hz), 3.8−3.95 (m, 4H), 4.92 (d, 1H, *J* = 7), (trans) 2.42 (dt, 1H, *J* = 4, 11 Hz), 4.7 (d, 1H, *J* = 5 Hz); IR 1705 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.7; H, 9.7.

8*β*-Hydroxy-8α-methylbicyclo[4.2.0]octan-7-one Ethylenketal (3c). Separated as an oil by column chromatography, eluting with a 7:3 cyclohexane ethyl acetate mixture: ^1H NMR *δ* 1.05 and 1.6 (two m, 2H), 1.3 (s, 3H), 1.35 and 1.65 (two m, 2H), 1.4 and 1.7 (two m, 2H), 1.45 (m, 2H), 1.92 (ddd, 1H, *J* = 3, 8, 9 Hz), 2.4 (ddd, 1H, 2, 8, 9 Hz), 3.0 (br s, 1H), 3.9−4.1 (m, 4H); a 5% NOE of the 1.92 *δ* signal was observed by irradiating the 1.3 *δ* singlet (3% enhancement for the 2.4 *δ* signal); ^{13}C NMR *δ* 20.0, 21.2, 21.8, 22.0, 22.1, 35.1, 38.0, 64.5, 65.6, 99.3, 113.1; IR 3470 cm^{-1}; MS *m/e* 155 (12), 116 (33), 99 (50), 55 (38), 43 (100). Anal. Calcd for $C_{11}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.2; H, 9.9.

8α-Hydroxy-8*β*-methylbicyclo[4.2.0]octan-7-one Ethylenketal (3c′). Obtained as a fraction impure of **3c** from the above chromatography: ^1H NMR *δ* 1.28 (s, 3H), 1.2−1.7 (m, 8H), 1.92 (ddd, 1H, *J* = 4, 8, 10 Hz), 2.5 (dt, 1H, *J* = 9, 10), 2.7 (br s, 1H), 3.9−4.1 (m, 4H); no NOE by irradiation of the

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1.28 δ singlet; ^{13}C NMR δ 18.2, 20.6, 21.1, 21.9, 22.1, 38.0, 38.5, 64.4, 65.3, 88.9, 110.9; IR 3485 cm^{-1}; MS *m/e* 116 (23), 99 (47), 55 (27), 43 (100).

2-[2-(1,3-Dioxolanyl)methyl]bicyclo[2.2.1]heptan-1-one (2d): bulb-to-bulb distilled (185 °C, 0.2 Torr); ^{1}H NMR δ 1.4 and 1.8 (two m, 2H), 1.38 and 1.62 (two m, 2H), 1.65 and 1.72 (two m, 2H), 1.55 (ddd, 1H, J = 5, 10, 14.5 Hz), 2.05 (dt, 1H, J = 4.5, 14.5 Hz), 2.25 (m, 2H), 2.6 (br d, 1H, J = 5 Hz), 2.7 (m, 1H), 3.85−4.0 (m, 4H), 4.98 (t, 1H, J = 4). Double irradiation experiments ensured that there is no long-range coupling between the signals at δ 1.65 and 1.72 (methylene at position 7) and the signal at δ 2.25 (methine at position 2), while this is normally observed when the hydrogen at position 2 is endo. Furthermore, an NOE is observed at 1.72 when irradiating at δ 2.25: ^{13}C NMR δ 21.3, 25.2, 30.1, 37.1, 39.1, 49.6, 50.0, 64.6, 64.8, 103.3, 219.2; IR 1743 cm^{-1}; MS *m/e* 87 (67), 73 (100). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32, H, 8.22. Found: C, 67.1; H, 8.3.

1-Hydroxytricyclo[4.2.1.0^{2,5}]nonan-3-one Ethylenketal (3d). Obtained as an impure fraction from the chromatography of the photolysate, using a 7:3 cyclohexane−ethyl acetate mixture as the eluant): ^{1}H NMR δ 1.3−2 (m, 9H), 2.2 (m, 1H), 2.3 (m, 1H), 3.0 (br s, 1H), 3.8−4.0 (m, 4H); ^{13}C NMR δ 22.0, 25.1, 30.6, 38.5, 40.8, 42.7, 44.2, 64.4, 64.6, 89.8, 109.2; IR 3485 cm^{-1}; MS *m/e* 94 (18), 87 (100).

3-Oxocyclohexancarboxyaldehyde ethylenacetal (2f): [24] bulb-to-bulb distilled (185 °C, 30 Torr); ^{1}H NMR δ 1.5−2.5 (m, 9H), 3.8−3.95 (m, 4H), 4.8 (d, 1H, J = 4 Hz); ^{13}C NMR δ 24.4, 25.4, 41.1, 41.3, 41.9, 64.9, 65.0, 105.6, 210.8; IR 1710 cm^{-1}. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.75. Found: C, 63.4; H, 8.7.

3-[2-(1,3-Dioxolanyl]-5-hexenal (4). Obtained as a fraction containing an unidentified impurity by bulb-to-bulb distillation (110 °C, 30 Torr): ^{1}H NMR δ 2.05−2.1 (m, 1H), 2.3−2.5 (m, 4H), 3.85−4.0 (m, 4H), 4.85 (d, J = 2 Hz), 5.05 and 5.12 (AB part of an ABX signal, 2H), 5.75 (m, 1H), 9.7 (d, 1H, J = 1 Hz); ^{13}C NMR δ 34.4, 37.2, 42.3, 64.8, 64.9, 105.1, 117.4, 135.5, 201.6; IR 1722 cm^{-1}.

3-Oxocycloheptancarboxyaldehyde ethylenacetal (2g): bulb-to-bulb distilled (185 °C, 0.2 Torr); ^{1}H NMR δ 1.35−1.65 (m, 3H), 1.9−2.65 (m, 6H), 2.4−2.6 (m, 4H), 3.85−4.0 (m, 4H), 4.75 (d, 1H, J = 4 Hz); ^{13}C NMR δ 24.3, 28.6, 31.1, 39.7, 43.7, 43.8, 65.0, 65.1, 106.5, 213.0. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.9; H, 8.8.

4-Oxo-2,2,6-trimethyl-5-heptenal ethylenacetal (2h): bulb-to-bulb distilled (160 °C, 0.2 Torr); ^{1}H NMR δ 1.05 (s, 6H), 1.88 (s, 3H), 2.12 (s, 3H), 2.42 (s, 2H), 3.85 and 3.95 (two m, 4H), 4.52 (s, 1H), 6.04 (br s, 1H); IR 1681 cm^{-1}; MS *m/e* 114 (34), 73 (100). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.1; H, 9.7. Photolysis of this compound gave a single main product, which did not accumulate above 10%, however. The mass spectrum was compatible with the structure of 2-hydroxy-2-(2-methyl-1-propenyl)-4,4-dimethylcyclobutanone ethylenketal (**3h**), *m/e* 184 (26), 114 (100), 113 (25), 99 (51). The base peak at *m/e* 114 corresponds to the retrocycloaddition observed in most of these ketals.

4-Oxo-4-phenylbutanal ethylenacetal (2i): [11a,25] bulb-to-bulb distilled (200 °C, 0.2 Torr); ^{1}H NMR δ 2.15 (dt, 2H, J = 4.5, 7 Hz), 3.15 (t, 2H, J = 7 Hz), 3.85−4.0 (m, 4H), 5.02 (t, 1H, J = 4.5 Hz), 7.45 (m, 2H), 7.55 (m, 1H), 7.98 (m, 2H); IR 1678 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.1; H, 6.9.

4-Oxo-2-phenylpentanal ethylenacetal (2j): bulb-to-bulb distilled (200 °C, 0.2 Torr); ^{1}H NMR δ 2.05 (s, 3H), 2.82 (dd, 1H, J = 8, 17 Hz), 3.02 (dd, 1H, J = 5.5, 17 Hz), 3.52 (ddd, 1H, J = 4, 5.5, 8 Hz), 3.8−3.95 (m, 4H), 5.02 (d, 1H, J = 4 Hz), 7.25 (s, 5H); IR 1715 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.6; H, 7.4. This product was recovered unchanged (<15% decomposition) after 12 h irradiation under the above condition.

2,4-Diphenyl-4-oxobutanal Ethylenacetal (2k). Separated by silica gel chromatography eluting with a 85:15 cyclohexane−ethyl acetate mixture: mp 88−91 °C (EtOH); ^{1}H NMR δ 3.38 (dd, 1H, J = 8, 17 Hz), 3.58 (dd, 1H, J = 5.5, 17 Hz), 3.78 (ddd, 1H, J = 4, 5.5, 8 Hz), 3.8−3.9 (m, 4H), 5.1 (d, 1H, J = 4 Hz), 7.3−7.45 (m, 5H), 7.4 (m, 2H), 7.5 (m, 1H), 7.95 (m, 2H); IR 1680 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.5; H, 6.5.

Acknowledgment. Partial support of this work by Consiglio Nazionale delle Ricerche, Rome, and MURST, Rome, is gratefully acknowledged.

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