Photochemical Reactions. LIX.[1] On the Mechanism of the Photodecarbonylation of β,γ-Unsaturated Aldehydes[2]

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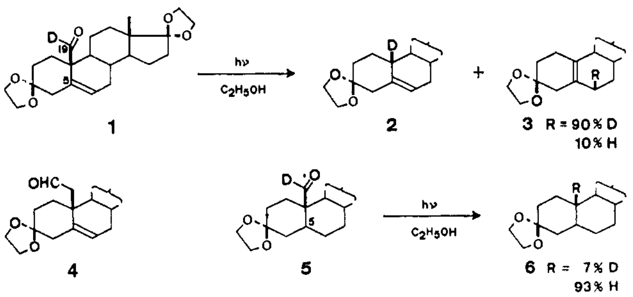
Abstract: Irradiation in the long-wavelength absorption bands of the β,γ-unsaturated aldehydes **7**, **8**, and **9** in various solvents results exclusively in decarbonylation from the singlet excited state. Fluorescence and singlet–triplet intersystem crossing have not been found to participate at the dissipation of excitation energy. The decarbonylation involves elimination of carbon monoxide and concurrent intramolecular transfer of the aldehydic hydrogen to the α- and γ-carbons, with the transfer to the α position dominating in all three aldehydes. An isotope effect of *ca.* 1.1 : 1 for the rates of decarbonylation of **8** and **8**-d_1 is observed. Added tri-*n*-butylstannane is capable of effecting both competition between intramolecular hydrogen transfer and incorporation of stannane hydrogen in the decarbonylation process, and competition between decarbonylation and reduction of the singlet excited aldehydes to the corresponding alcohols. The quantum yields for decarbonylation of aldehydes **7** and **8** are solvent dependent, averaging *ca.* 0.5. In *t*-butyl alcohol, the values are independent of wavelength ($\phi_{-\text{CO}}{}^{2970} \simeq \phi_{-\text{CO}}{}^{3130}$), but they exhibit wavelength-dependent variations in apolar solvents ($\phi_{-\text{CO}}{}^{2970} < \phi_{-\text{CO}}{}^{3130}$). Wavelength dependencies are also observed for the ratio of intramolecular hydrogen transfer to the α- and γ-carbons (α/γ at 2804 Å > α/γ at 3341 Å), and of the extent of incorporation of stannane hydrogen (incorporation at 2804 Å > incorporation at 3341 Å) in the decarbonylation process. While a concerted process is not excluded for the major decarbonylation path, the intramolecular hydrogen transfer to the α-carbon, α cleavage of the aldehydic rotamers to individual allyl–formyl radical-pair intermediates as the primary photochemical process is seen to account for the entire reaction pattern. The secondary reactions of these postulated radical pairs would depend on the incipient orientation of the radical partners within as preformed in their rotameric aldehyde precursors. Conformations associated in **7**–**9** with homoconjugation and unimolecular photodecarbonylation are not possible in the bridged aldehyde **10**. The photoexcited compound does not decarbonylate, but rather shows preference for singlet–triplet intersystem crossing and reactions from the triplet state—photoreduction to alcohol and homologization to the corresponding methyl and ethyl ketones (in pentane), a novel photochemical aldehyde transformation.

The photodecarbonylation of β,γ-unsaturated aldehydes was encountered in our studies of photochemical transformations in steroids[3] and was subsequently investigated in some detail with androst-5-en-19-al derivatives.[4] The irradiation of these aldehydes resulted in a quantitative chemical yield of the corresponding isomeric 5(6)- and 5(10)-olefins in the approximate ratio 19 : 1 (Chart I). By the use of deuterioaldehydes (*cf.* **1**) and by appropriate scrambling experiments it was shown[4b] that the photolytic decarbonylation in ethanol solution involves a fully intramolecular incorporation of the aldehydic deuterium atom in the case of the major product **2**. In the formation of the minor component **3**, hydrogen uptake from the solvent competes to the extent of 10%[5] with the intramolecular deuterium transfer. Evidence for the important influence which β unsaturation exerts on the intramolecular hydrogen transfer in this decarbonylation process was obtained upon irradiation of the γ,δ-unsaturated homolog **4** and the saturated 5α- and 5β-aldehydes **5**. In contrast to the results with **1**, the still appreciable decarbonylation to **6** evidently involves a free-radical α cleavage (Norrish type I process) and hydrogen incorporation from the solvent. **4** showed no detectable tendency toward decarbonylation. Both aldehydes, **4** and **5**, formed *sec*-alcohols through intramolecular hydrogen abstractions as alternative photochemical processes.

Chart I. Earlier Results. Irradiation of Steroidal Aldehydes



The present investigation had as its goal a further probe into the scope of this photoreaction, the determination of the gross reaction route(s), the reaction efficiency, and the multiplicity of the reactive state(s). In particular, results with the β,γ-unsaturated aldehydes **7**, **8** (laurolenal), **9**, and **10** are reported.[6] The three compounds **7**–**9**, as well as **1**, have n → π^* absorptions which, on comparison with the corresponding transitions of saturated aldehydes, are distinctly displaced toward longer wavelengths, enhanced in intensity, and exhibit no or negligible hypsochromic shifts upon increase of solvent polarity. These data,

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[1] For paper LVIII of the series, see S. Domb and K. Schaffner, *Helv. Chim. Acta*, **53**, 677 (1970).

[2] Taken in part from the Doctoral Dissertation of E. Baggiolini, ETH, Zürich, 1969.

[3] For a recent review note O. Jeger and K. Schaffner, *Pure Appl. Chem.*, in press.

[4] (a) J. Iriarte, J. Hill, K. Schaffner, and O. Jeger, *Proc. Chem. Soc.*, 144 (1963); (b) J. Hill, J. Iriarte, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 292 (1966).

[5] Deuterium analyses were performed by mass spectrometry in both the previous[4b] and the present investigation, with a standard error of ±1%.

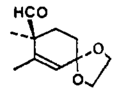
[6] Preliminary communications on part of this work: ref 3 and 4b; K. Schaffner, *Chimia*, **19**, 575 (1965); E. Baggiolini, H. P. Hamlow, K. Schaffner, and O. Jeger, *ibid.*, **23**, 181 (1969); K. Schaffner in "Reactivity of the Photoexcited Organic Molecule," Interscience, New York, N. Y., 1967, p 326; Plenary Lecture at the Meeting of the Société Chimique de France, March 1969, Paris.

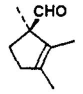
Table I. Spectral Data of Aldehydes **1**, 7, **8**, 9, and **10**

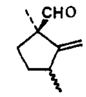
Aldehyde	Uv-absorption[a] solvent	λ, Å	ϵ_{max}	Circular dichroism solvent	Temp, °C	λ, Å	$\Delta\epsilon_{max}$	$I_{T_1}^{T_2}$, %[b]	Lit.
1	Ethanol	2260	1255	Methylcyclohexane–isopentane, 1:3	+20	3090	−10.12	−27	*c*, *d*
		3100	113			3185	−9.54		
				Methylcyclohexane–isopentane, 1:3	−178	3080	−13.68		
						3175	−13.88		
(±)-7	Ethanol	3080	103						This work
	Isooctane	3020	118						
(+)-**8**	Ethanol	2280	1630	Methylcyclohexane–isopentane, 1:3	+20	3005	+10.30	−43	*d*
		3050	135	Methylcyclohexane–isopentane, 1:3	−180	3135	+17.31		
	Isooctane	3050	132			3045	+18.16		
(±)-**9**	Ethanol	2965	71						This work
	Isooctane	2990	62						
10	Ethanol	2980	10						This work
	Isooctane	3020	24						

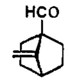
[a] All measurements at +20° and an absorbance of 0.5–0.8. [b] Relative change of Δϵ on temperature decrease; *cf.* G. Snatzke, *Proc. Roy. Soc., Ser. A*, **297**, 43 (1967). [c] Reference 4. [d] Reference 10.

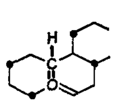
including concurrent $\pi \rightarrow \pi^*$ transitions in the region of 2200–2300 Å (see Table I), are indicative of homoconjugation between the aldehyde carbonyl and the double bond, attributable to overlap of the C=C π cloud with the nonbonding p and the π^* orbitals of the carbonyl.[4,7,8] Unlike the situation in the aldehydes **1** and **7**–**9**, the geometry of the bridgehead aldehyde **10** is clearly less favorable for a similar electronic interaction. This is reflected in the relatively low intensity and short wavelength position of the $n \rightarrow \pi^*$ absorption. The inherent dissymmetry of the chromophore resulting from homoconjugation is further substantiated in the circular dichroism data of the optically active aldehydes **1** and **8**. They show characteristically[9] pronounced ellipticities with a similar strong-temperature gradient.[10] These results have been interpreted in terms of A (with ring B in a twist form) as the conformation of **1** which is both the most stable form and favorable for a dissymmetric orbital overlap.[10] Correspondingly, B represents an important homoconjugated contributor to the rotamer population of (*R*)-(+)-laurolenal (**8**).[11]

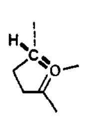

(±)-**7**


(+)-**8**


(±)-**9**


10


A


B

Results

Preparation of the Aldehydes (See Chart II). The racemic aldehydes **7** and **7**-d_1 (deuterium content 97%[5]) were synthesized from Hagemann's ester (**11**).[12] Ketalization to **12** and subsequent reduction in separate runs with lithium aluminum hydride and deuteride afforded the alcohols **13** and **13**-d_2, respectively. Oxidation with Sarrett's reagent (chromic oxide in pyridine) to the aldehydes **14** and **14**-d_1 was followed by alkylation using methyl iodide and potassium *t*-butoxide.

Dextrorotatory laurolenal (**8**) and its deuterated form **8**-d_1 (deuterium content 100%[5]) are available from methyl (+)-laurolenoate (**16**)[13] in 76% yield by lithium aluminum hydride and deuteride reduction to **18** and **18**-d_2, respectively, and subsequent oxidation with sulfur trioxide–pyridine complex in dimethyl sulfoxide and triethylamine.[14] The enantiomeric purity of the aldehyde (+)-**8** was analyzed by two independent methods: (1) by comparison of the [α]D values of an aldehyde sample obtained as above, and of a second sample which had been prepared from the same (+)-laurolenic acid (**15**) batch (**15** was converted to the acid chloride **17** and esterified with testosterone; crystallization of the ester to a constant melting point was followed by lithium aluminum hydride reduction to laurolenol (**18**) and oxidation to (+)-**8** as above); (2) by the isotope dilution method[15] using a mixture of (+)-laurolenol (**18**) and (±)-trideuteriolaurolenol (**18**-d_3; *vide infra*).[16] The composition of the mixture was altered by repeated crystallizations of the 3,5-dinitrobenzoate derivative of the entire sample and subsequent hydrolysis of the ester crystallizate. The

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(7) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959).

(8) Molecular models show that orbital overlap between the C=C and C=O groups in the β,γ-unsaturated aldehydes should be greatest in a conformation (*cf.* projections A and B) where the nonbonding p orbital of the oxygen and the π axis approximate a parallel, and the two π systems a perpendicular orientation. While the aldehydes can adopt such a conformation freely by rotation around the C_α–CHO bond, the rigid orientation of the corresponding groups in the β,γ-unsaturated ketones which have been studied so far[9] deviates notably from such an alignment.

(9) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962); A. Moscowitz, A. E. Hansen, L. S. Forster, and K. Rosenbeck, *Biopolym. Symp.*, 75 (1964); A. Moscowitz, *Proc. Roy. Soc. London, Ser. A*, **297**, 40 (1967); E. G. Höhn and O. E. Weigang, Jr., *J. Chem. Phys.*, **48**, 1127 (1968).

(10) G. Snatzke and K. Schaffner, *Helv. Chim. Acta*, **51**, 987 (1968).

(11) The sign of the Cotton effect of (+)-laurolenal (8) confirms independently the *R* chirality which has been established previously by Woodward and coworkers using a different approach. We thank Professor R. B. Woodward for this private communication; *cf.* R. B. Woodward, *Pure Appl. Chem.*, 17, 519 (1968); see also W. L. Meyer, A. P. Lobo, and E. J. Marquis, *J. Org. Chem.*, 30, 181 (1965).

(12) C. T. Hagemann, *Ber.*, 26, 876 (1893).

(13) See Meyer, *et al.*, ref 11.

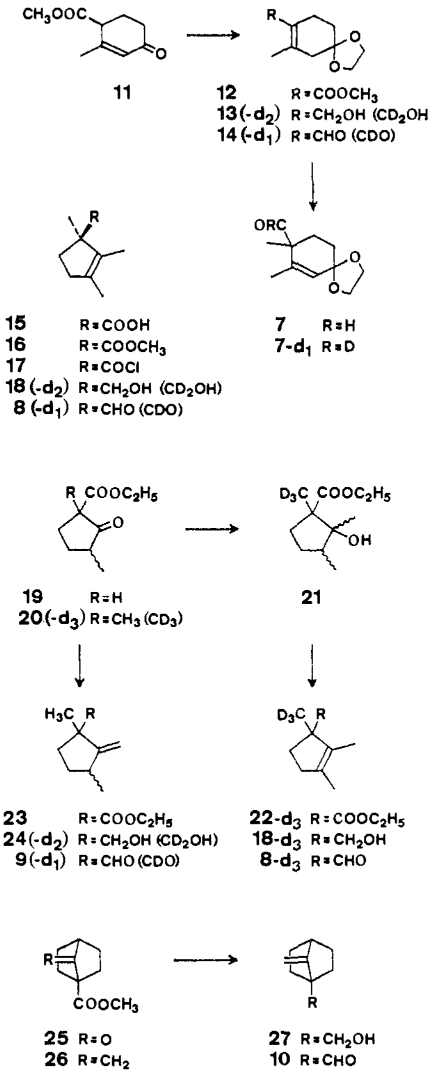
(14) *Cf.* J. R. Parikh and W. v. E. Doering, *J. Amer. Chem. Soc.*, **89**, 5505 (1967).

(15) H. Gerlach, *Helv. Chim. Acta*, **49**, 2481 (1966), and references therein. We thank Dr. H. Gerlach for helpful discussions relating to the application of the isotope dilution analysis.

(16) The choice of laurolenol (18) as the substrate in the isotope dilution experiment was made after several exploratory attempts using other derivatives proved less satisfactory for various reasons; *e.g.*, the system of the mixed cyclohexylammonium salts of (+)-laurolenic acid (15) and (±)-laurolenic acid-d_3 was abandoned because the purification of the acid mixture for the optical rotatory measurement with an acceptable range of experimental error required too large amounts of material.

analysis is based on the determination of the optical rotatory power and the isotopic composition of the laurolenol mixture[17] before and after the esterification–crystallization–hydrolysis cycle. The enantiomeric purity of the (+)-laurolenal used in the photolyses (**8**, $[\alpha]^{22}{}_{D}$ +597 ± 5.8° (*c* 1.5, $CHCl_3$)), as determined by methods 1 and 2, was 95.6 ± 1.7% and 96.3 ± 1.4%, respectively.

Chart II. Preparation of the Aldehydes



The synthesis of the racemic trideuteriolaurolenal **8**-d_3 was based on an experimental modification of the procedure described by Meyer, *et al.*,[11] for the preparation of the racemic methyl laurolenoate (see also Experimental Section). Base-catalyzed alkylation of the keto ester **19** in separate runs with methyl iodide and trideuteriomethyl iodide gave mixtures of *cis*- and *trans*-**20** and -**20**-d_3, respectively. **20**-d_3 was converted to **21** by a Grignard reaction, and dehydration of the tertiary alcohol on heating in the presence of iodine gave quantitatively **22**-d_3. The keto ester **20** served also as the key intermediate in the preparation of the aldehydes of type **9**. Wittig reaction with salt-free ylide solution[18] occurred almost selectively with one of the components of the stereoisomeric keto ester mixture (**20**), forming an unsaturated ester **23** of still unknown configuration. Wittig reaction under identical reaction conditions with keto ester **25** furnished product **26**. For the conversion of the esters **22**-d_3, **23**, and **26** to the aldehydes (±)-**8**-d_3, (±)-**9**, (±)-**9**-d_1, and **10**, the same reaction conditions were employed as specified above for the corresponding sequences leading to (+)-**8** and (+)-**8**-d_1.

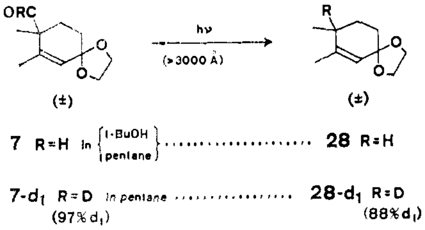
Ultraviolet Irradiation of Aldehydes (±)-7 and (±)-7-d_1 (See Chart III). The cyclohexenyl aldehyde **7** approximates a monocyclic analog of the steroidal Δ^5-19-aldehyde (*cf.* **1**). Photolysis of **7** resulted in a smooth decarbonylation to compound **28** as the sole photoproduct, with quantum yields as listed in Table II. The nmr spectrum of product **28** shows doublets at δ 1.01 (*J* = 7 cps) and 1.67 (*J* = 1.5 cps) for the secondary and the olefinic methyl groups, respectively, and a finely split olefinic proton signal at δ 5.19. Acid-catalyzed hydrolysis of **28** gave 3,4-dimethylcyclohex-2-enone which was further characterized as its known semicarbazone.[19] The photodecarbonylation of the deuterated aldehyde **7**-d_1 in pentane is accompanied by the incorporation of 9% hydrogen from the solvent in the photoproduct **28**-d_1. The position of the retained deuterium atom is located by the nmr spectrum of the product in which the appropriate proportion of the secondary methyl signal at δ 1.01 has collapsed to a singlet.

Table II. Quantum Yields of the Photodecarbonylation of Aldehydes 7 and 8[a]

Aldehyde	Solvent	Quantum yield at wavelength 3130 Å	2970 Å
7	Hexane	0.55	0.42
	t-Butyl alcohol	0.44	0.44
8	Hexane	0.61	0.54
	Benzene	0.39	0.32
	t-Butyl alcohol	0.44	0.43

[a] Estimated error ±0.02. Irradiations at room temperature with 6.105 μEinsteins/min at 3130 Å and 3.437 μEinsteins/min at 2970 Å. Aldehyde conversions 20–40%.

Chart III. Photolysis of Aldehydes (±)-7 and (±)-7-d_1



Irradiation of Laurolenals *R*-(+)-8, *R*-(+)-8-d_1, and (±)-8-d_3 (See Charts IV and V). (*R*)-Laurolenal (**8**) decarbonylates readily to optically active, levorotatory 1,2,3-trimethylcyclopentene (**29**) on irradiation in its long-wavelength absorption band. Parallel photolytic

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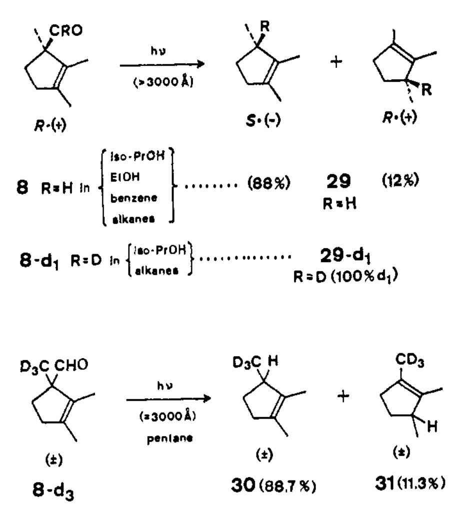
[17] The analyses of the composition of the mixture of (+)-18 and (±)-18-d_3 prior to the crystallization of its 3,5-dinitrobenzoate by optical rotatory measurement and by mass spectrometry were in perfect agreement with the values calculated from the appropriate proportional contributions of the respective components. This precludes the *a priori* possibility of a nonlinear relationship between the rotatory power and the enantiomeric composition of **18**, and thus confirms the applicability of optical rotatory measurements in this isotope dilution analysis.

[18] *Cf.* G. Wittig, H. Eggers, and P. Duffner, *Ann. Chem.*, **619**, 10 (1958); H. J. Bestman, *Angew. Chem.*, 77, 609 (1965).

[19] H. E. Baumgarten and R. E. Eifert, *J. Org. Chem.*, **18**, 1177 (1953).

runs in isopropyl alcohol, ethanol, benzene, and alkane solvents (pentane, hexane) showed very similar reaction rates, and no additional photoproducts were detectable by vapor phase chromatography in any of these solvents. The quantum yields for the photolyses in *t*-butyl alcohol, benzene, and hexane with 2970- and 3130-Å radiation are given in Table II.

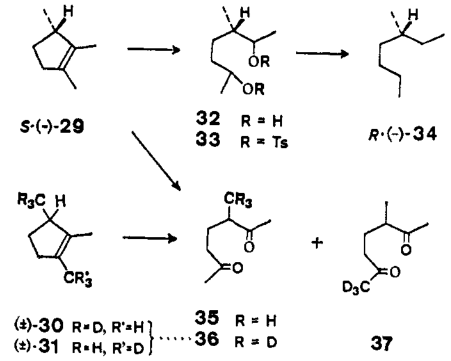
Chart IV. Photolysis of Laurolenals *R*-(+)-**8**, *R*-(+)-**8**-d_1, and (±)-**8**-d_3



The rotatory power of aldehyde **8** was unchanged within ±0.8% of the initial value after incomplete photochemical conversions of up to 55%. Also, attempts of sensitization of photoproduct **29** in benzene and toluene solutions with 2537-Å radiation[20] did not affect its optical activity, nor was any other transformation observed.

Both the enantiomeric purity of the photoproduct **29** and the chiral assignment were determined by degradation of **29** to 3-methylheptane (**34**) whose *S*-(+) enantiomer has been described by Lardicci.[21] (*R*)-Laurolenal (**8**) was photolyzed in pentane solution through a Pyrex filter until the conversion to **29** was complete. The solution was then ozonized directly at −70° and subsequently treated with lithium aluminum hydride. The resulting diol **32** was converted to the ditosylate **33** which was reduced with lithium aluminum hydride to a levorotatory hydrocarbon. Direct comparison with commercially available racemic 3-methylheptane and with a sample of authentic *S*-(+) enantiomer[21,22] established that the degradation product was (*R*)-3-methylheptane (**34**) of an enantiomeric purity of 72.6 ± 1.5%. We may therefore conclude that the overall reaction leading to hydrogen addition to the trimethylcyclopentenyl moiety in the photolysis of **8** (96% enantiomeric purity) proceeds with *ca.* 24% racemization, *i.e.*, it involves either (1) 76% of a stereospecific process with retention of chirality and 24% of racemization through a random hydrogen addition mode or (2) a fully stereospecific process composed of 88% retention and 12% inversion. Separate experiments with monochromatic light showed that the degree of stereospecificity is somewhat wavelength dependent. Thus, the optical activity of **29** resulting with 3341-Å radiation was 94% of the activity obtained with 2804 Å.

Chart V. Degradation of the 1,2,3-Trimethylcyclopentene Photoproducts (−)-**29**, (±)-**30**, and (±)-**31**



The photolytic decarbonylation of the deuterated *R*-aldehyde **8**-d_1 in isopropyl alcohol or alkane solutions furnished deuterated trimethylcyclopentene with full retention of the isotopic composition of the starting material. Structure **29**-d_1 for this photoproduct is evident from its nmr spectrum in which the signal of the secondary methyl group at δ 0.97 appears as a singlet. In a competitive experiment using an equimolar mixture of compounds **8** and **8**-d_1 in pentane, the relative rates of disappearance of aldehydes and of formation of products **29** and **29**-d_1 were 1.0:1.0–1.06 and 1.14:1.0, respectively, as measured by mass spectrometric analysis of the appropriate vapor phase chromatographic fractions of aliquots which had been removed periodically during the photolysis.

Irradiation of the racemic trideuteriomethyl aldehyde **8**-d_3 in pentane through Pyrex gave a mixture of 88.7 ± 0.5% 3′-d_3 (**30**) and 11.3 ± 0.5% 1′-d_3 trimethylcyclopentene (**31**). The photolyzed solution was directly ozonized at −70°,[23] and the ozonide was hydrogenated catalytically to give the diketones **36** and **37**. By careful integration of the methyl signals in the nmr spectrum (see Figure 2, Experimental Section) and comparison with the spectral data of nondeuterated 3-methylheptane-2,6-dione (**35**), which was obtained from **29** by a similar degradation, the photoproduct was found to consist of 88.7 ± 0.5% **36** and 11.3 ± 0.5% **37**. This result was confirmed by the treatment of the mixture with alkali, upon which a fraction of 12%[5] (*i.e.*, compound **37**) was subjected to deuterium–hydrogen exchange and converted to the d_0 diketone **35**.

In a further photochemical experiment a pentane solution of 0.288 *M* **8**-d_1 and 0.284 *M* **8**-d_3 was irradiated. Mass spectral analysis of the photomixture established the exclusive presence of d_1 and d_3 cyclopentenes (**29**-d_1, **30**, **31**). Scrambling and formation of d_0 (**29**) and d_4 cyclopentenes had not occurred.

Irradiation of Aldehydes (±)-9 and (±)-9-d_1 (See Chart VI). The photolysis of aldehyde **9**, a double

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[20] For possible mechanisms for racemization of the photosensitized cyclopentene (−)-**29**, see P. J. Kropp, *J. Amer. Chem. Soc.*, **89**, 3650 (1967).

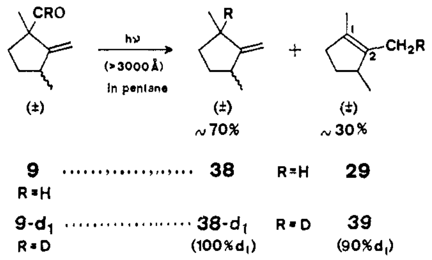
[21] L. Lardicci, *Gazz. Chim. Ital.*, **91**, 458 (1961).

[22] We thank Professor P. Pino for a sample of (*S*)-(+)-methylheptane.

[23] A direct determination of the composition of the mixture of photoproducts **30** and **31** using spectrometric methods proved unsatisfactory; *e.g.*, the appropriate methyl signals in the nmr spectrum were not sufficiently separated from other resonances to allow a reliable integration, and test runs in the mass spectrometer indicated that a quantitative estimate of **30** and **31** is not possible using the $M^+ - 15$ and $M^+ - 18$ peaks which are due to the facile loss of the allylic methyl and trideuteriomethyl groups, respectively. In fact, a ratio of 59:41 for $(M^+ - 18):(M^+ - 15)$ was observed with the photomixture containing 88.7% **30** and 11.3% **31** (see Figure 3B, Experimental Section).

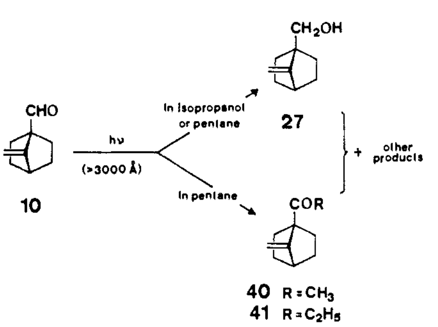
bond isomer of laurolenal (**8**), in pentane led exclusively to decarbonylation. The photoproducts were two olefinic isomers in an approximate ratio 7:3, resulting from hydrogen incorporation at the former formyl-bearing α carbon (**38**) and at the γ position (**29**). Product **38** is characterized in the nmr by a doublet at δ 1.05 ($J = 6.5$ cps) of the two secondary methyl groups, and by a triplet at δ 4.73 ($J = 2.5$ cps) of the two olefinic methylene protons. The irradiation of the deuterioaldehyde **9**-d_1 in pentane furnished the corresponding two products, **38**-d_1 with no loss of deuterium, and **39** with a loss of 10% of the initial deuterium content. The position of the deuterium atom in **39** is located by mass spectrometry in the methyl group at C-2. The base peak at *m/e* 96, which corresponds to the fragment $M^+ - 15$ of monodeuterated **39**, is accompanied only by 6% of $M^+ - 16$ attributable to the elimination of CH_2D radical (presumably occurring subsequent to the allylic rearrangement of a methylene ring hydrogen which should be less favorable than the rearrangement of the methine hydrogen) (see Figure 3C, Experimental Section, for the mass spectrum). From previous data[23] a CH_2D elimination from the olefinic position C-1 would be expected to amount to about 30% of the total loss of methyl and can therefore be eliminated from further consideration.

Chart VI. Photolysis of Aldehydes (±)-**9** and (±)-**9**-d_1



Irradiation of Aldehyde 10 (See Chart VII). The irradiation of aldehyde **10** in pentane furnished a complex product mixture, of which only the three major components **27**, **40**, and **41** were characterized sufficiently. The remaining products consisted, *inter alia*, of several distinctly more volatile compounds as well as of material which was insoluble in pentane. The two ketones **40** and **41**, which amounted only to *ca.* 10 and 6%, respectively, of the yield of alcohol **27**, exhibited the appropriate ir (ν_{CO}, $\nu_{C=C}$, and $\nu_{=CH_2}$) and nmr data ($\delta_{C=CH_2}$, δ_{COCH_3}, and $\delta_{COCH_2CH_3}$) of the acyl side chain and the ethylidene bridge partial structures. The prominent mass spectral peaks were M^+ (*m/e* 150, $C_{10}H_{14}O$), $M^+ - 15$, $M^+ - 28$, $M^+ - 43$, $M^+ - (43 + 28)$, and *m/e* 43 (base peak) for **40** and M^+ (*m/e* 164, $C_{11}H_{16}O$), $M^+ - 28$, $M^+ - 29$ (base peak), $M^+ - 57$, $M^+ - (57 + 28)$, and *m/e* 57 for **41**.

Chart VII. Photolysis of Aldehyde **10**



The photolysis of **10** in degassed isopropyl alcohol solution resulted almost entirely in reduction and formation of alcohol **27**.

Multiplicity of the Reactive Excited States. Laurolenal (**8**) exhibits neither fluorescence (at room temperature) nor phosphorescence (at 77°K; both measurements in 0.01 *M* solutions) upon excitation in the 2800–3400 Å region. Attempts to obtain indirect spectroscopic information on the excited triplet state of this aldehyde were equally unsuccessful. Irradiation with wavelengths of 3350–3400 Å of a 0.01 *M* solution of **8** in EPA containing 0.1 *M* naphthalene at 77°K did not sensitize phosphorescence from naphthalene, nor was the acetophenone (0.001 *M*) phosphorescence quenched on irradiation with 2800 Å in EPA at 77°K on admixture of 0.1 *M* **8**.

Accordingly, an attempt to sensitize the decarbonylation of **8** (0.15 *M*[24]) with 4.2 *M* acetophenone in pentane and >3000-Å radiation failed, and the aldehyde remained unchanged. When a 0.18 *M* benzene solution of **8** was irradiated with light of 2537 Å, a slow consumption of the aldehyde and *partial* conversion to the decarbonylation product **29** (corresponding to *ca.* two-thirds of the reacted starting material) were observed.[28]

However, irradiation at 2537 Å of a 0.145 *M acetone solution* of **8** resulted in a complete consumption of the aldehyde, with only a negligible amount of trimethylcyclopentene **29** formed. Products of longer retention times than **29** could not be detected by vpc screening, which rules out the formation of compounds of substantially higher molecular weight as resulting, *e.g.*, from addition reactions of acetone to **8** or **29**.[29]

Experiments designed to effect quenching of any decarbonylation of **8** in its excited triplet state involved irradiations with wavelengths above 3270 Å of 0.1 *M* hexane solutions of aldehyde containing 0.5 and 1.0 *M* naphthalene and 0.02–5.0 *M* *cis*-1,3-pentadiene, respectively. In an additional run, a 0.1 *M* solution of **8** in neat *cis*-1,3-pentadiene was photolyzed. In neither experiment did the rate of aldehyde decarbonylation and formation of **29** differ from that of a parallel run in hexane alone, nor could a *cis–trans* isomerization of pentadiene through sensitization by excited triplet aldehyde be observed.

(24) The concentrations of aldehyde and acetophenone were adjusted so that acetophenone absorbed more than 98% of the incident light. The resulting rate constant (*ca.* 10^8–10^9 sec^{-1}) for diffusion-controlled collisions[25] between aldehyde and acetophenone molecules is too small for efficient singlet transfer,[25] yet sufficiently high to ensure collision of triplet exited acetophenone molecules with aldehyde in view of the rate constants of at least 10^{10} sec^{-1} for the unimolecular decay of excited acetophenone singlet[26] and *ca.* 10^5 sec^{-1} for the triplet destruction in solution.[27]

(25) Note F. Wilkinson (*Advan. Photochem.*, **3**, 241 (1964)) for a summary of diffusion rates and for arguments against long-range transfer of singlet excitation between n,π* acceptor and donor transitions.

(26) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

(27) S. G. Cohen, D. A. Laufer, and W. Sherman, *J. Amer. Chem. Soc.*, 86, 3060 (1964).

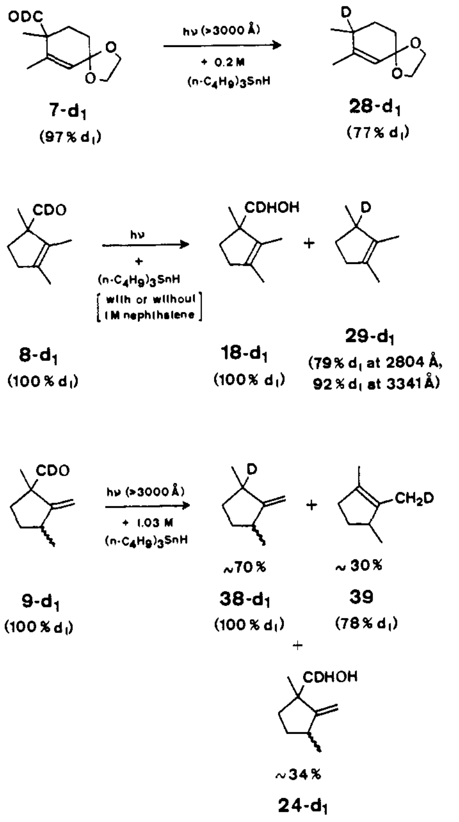
(28) It seems possible that both singlet and triplet energy transfer processes are responsible for the conversion of aldehyde observed in this experiment, albeit either process is quite inefficient when compared to the high quantum yields on direct irradiation of 8.

(29) An investigation is in progress into the possibility that the major acetone-sensitized reaction of **8** parallels the rearrangement of the corresponding methyl ketone **43** under identical irradiation conditions (see Discussion, footnote 35, and E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969)).

Similarly, the photodecarbonylation of aldehyde **7** was not affected in neat 1,3-pentadiene, and no reaction was observed upon irradiation of **7** in benzene with 2537 Å. On the other hand, quenching of the photoreactivity of aldehyde **10** in isopropyl alcohol was observed already at relatively moderate 1,3-pentadiene concentrations (10^{-2}–10^{-1} *M*).

Irradiations in the Presence of Tri-*n*-butylstannane (See Chart VIII). When solutions of the aldehydes **8** and **8**-d_1 in pentane containing tri-*n*-butylstannane were photolyzed with wavelengths >3270 Å, reduction to the alcohols **18** and **18**-d_1, respectively, competed with decarbonylation. In addition, the decarbonylation of **8**-d_1 occurred with partial incorporation of a stannane hydrogen into product **29**-d_1 at the expense of the intramolecular transfer of the aldehydic deuterium. Regeneration of unreacted aldehyde **8**-d_1 after a 50% conversion in the presence of 2.17 *M* stannane showed that no deuterium–hydrogen exchange had intervened. The extent of hydrogen uptake from the external source into **29**-d_1 remained practically constant in the range of 0.34 *M* (*ca.* 0.5 mol equiv; 91.2% $d_1{}^5$ for **20**-d_1) to 2.17 *M* stannane (90.5% $d_1{}^5$). Moreover, the isotopic composition of **29**-d_1 as well as the ratio of the products **18**-d_1 and **29**-d_1 (*ca.* 1.3:1 at 0.34 *M* stannane) were insensitive to the addition of up to 1 *M* naphthalene. Experiments with monochromatic light indicated that in fact the incorporation of stannane hydrogen into **29**-d_1 is wavelength dependent, amounting to 21% at 2804 Å and 8% at 3341 Å and 1 *M* stannane.

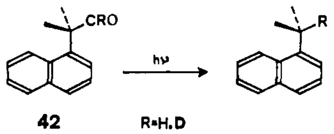
Chart VIII. Photolysis of Aldehydes (±)-7-d_1, (+)-**8**-d_1, and (±)-**9**-d_1 in the Presence of Tri-*n*-butylstannane



The incorporation of external hydrogen in the decarbonylation process (at >3000 Å) of the aldehydes **7**-d_1 and **9**-d_1 increased from 9% in **28**-d_1 and 10% in **39** in pure pentane solutions to 20 and 22%, respectively, when the photolyses were conducted in the presence of tri-*n*-butylstannane (stannane concentrations 0.2 *M* with **7**-d_1 and 1.03 *M* with **9**-d_1). On the other hand, the initial isotope content was again retained fully in the decarbonylation of **9**-d_1 to product **38**-d_1. Here, photoreduction to the corresponding alcohols competed also with decarbonylation, leading, *e.g.*, in the case of **9**-d_1, to a *ca.* 2:1 ratio of decarbonylation (**38**-d_1 and **39**) and reduction products (**24**-d_1).

Discussion

Multiplicity of the Reactive Excited State Responsible for Decarbonylation and for Reduction with Tri-*n*-butylstannane of Aldehydes 7, 8, and 9. The virtually complete difference in product patterns formed upon direct irradiation of laurolenal (**8**) and upon sensitization with acetone excludes unequivocally the lowest triplet of the aldehyde[30] as the reactive state in the decarbonylation **8** → **29**, and it is strong support for a *singlet excited state reaction.* Corroborative evidence is gained from the finding that the decarbonylation (of **7** and of **8**) is not affected by relatively high concentrations of naphthalene and 1,3-pentadiene (including *neat* pentadiene) which are generally efficient quenchers of carbonyl triplets.[32] The *a priori* fortuitous possibility that decarbonylation occurs from a higher lying triplet state of **8**, *i.e.*, of higher energy than triplet excited acetone, appears unlikely. It is rejected in view of the fact that in the presence of tri-*n*-butylstannane photoreduction to alcohol **18** can compete with decarbonylation. This reaction is equally unaffected by naphthalene. The bimolecular nature of the reduction demonstrates that the reactive excited state of laurolenal (**8**) is amenable to diffusion-controlled processes.[33] This excludes decarbonylation from an upper triplet state at a faster than diffusion-controlled rate, and thus renders the negative results of the triplet quenching experiments meaningful.



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That singlet–triplet intersystem crossing does not participate noticeably at the energy dissipation of singlet excited laurolenal (**8**) is documented already by the diverse results of direct and sensitized irradiations of **8**. Further evidence for the lack of triplet population on direct excitation is found in the absence of both

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(30) The failure of acetophenone to induce any sensitized photochemical conversion (as well as the observation that 8 is not capable of quenching the phosphorescence of acetophenone) on one hand, and the successful sensitization with acetone on the other hand, place the lowest triplet state of laurolenal (8) between 73.6[31a] and 82 kcal/mol[31b] (E_T of acetophenone and acetone, respectively).

(31) (a) See J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 298; (b) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(32) It is of interest to note in this connection that, in accordance with the assignment of the singlet multiplicity to the photodecarbonylation of β,γ-unsaturated aldehydes, the naphthylacetaldehyde **42** undergoes a strictly analogous reaction (H. Wolf and K. Schaffner, unpublished work).

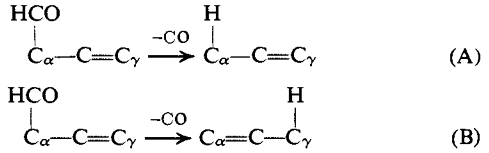
(33) The argument is based on the assumption that both decarbonylation and reduction of laurolenal (8) occur from the same excited state. With a quantum yield of 0.61 for the formation of 29 in hexane, and a ratio of 1:1.3 for decarbonylation (29) and reduction products (18) in the presence of 0.34 *M* tri-*n*-butylstannane, this point seems sufficiently secure.

phosphorescence emission from the aldehyde and laurolenal-sensitized phosphorescence from admixed naphthalene. Inefficiency of the singlet–triplet intersystem crossing has been noted recently for several cyclic β,γ-unsaturated ketones[34] as well as for the methyl ketone homolog of laurolenal, **43**, and related ketones.[35]

Laurolenal (**8**) as well as the corresponding methyl ketone **43** do not fluoresce at room temperature. Deactivation of the singlet excited state is therefore restricted to nonradiative internal conversion to the ground state and photochemical reactions. In both cases (*vide infra* for the discussion of **8**) α cleavage processes to acyl and allyl radicals contribute at least in part to the photoreactivity. Reversal of these primary photoreactions by rapid radical recombination may thus provide for some of the apparent nonphotochemical pathways (*i.e.*, for part of $1 - \phi_{-\mathrm{CO}}$ in **8** → **29**). In view of the relatively high quantum yields observed for decarbonylation (see Table II for $\phi_{-\mathrm{CO}}$), the (sum of) primary photochemical reaction(s) of **8** (reversal of α cleavage and decarbonylation) may in fact account for almost the entire dissipation of excitation energy. Circumstantial support for this point is found in the failure of laurolenal (**8**) to add to *trans*-1,2-dicyanoethylene (0.11 *M* in ether) on irradiation[36] and to sensitize biacetyl (10^{-2} *M*) fluorescence (isopentane solution, irradiation at 2900–3100 Å).

The photoreduction of laurolenal (**8**), the first example of a bimolecular carbonyl reduction in the singlet excited state,[37] contrasts strikingly with the observation that, even in the presence of stannane, photoreduction of saturated and conjugated ketones occurs exclusively in the triplet state.[39] If it is assumed that α-cleavage processes (including decarbonylation) and reduction by stannane are the only deactivation modes of excited **8**, the rate constant for reduction in the experiment with 0.34 *M* stannane is $k_{\mathrm{red}} \sim 2.3k_{\alpha}$.[40] With k_{α}, the rate constant of α cleavage, approaching the rate of diffusion, 10^9 sec^{-1}, k_{red} approximates $2.3 \times 10^9\ M^{-1}$ sec^{-1}. This value is in the same order of magnitude as that of the reduction rate constant of triplet acetone and stannane ($8 \times 10^8\ M^{-1}$ sec^{-1}).[39b]

Reaction Pathways of Decarbonylation. The experimental findings of this study on the photodecarbonylation of β,γ-unsaturated aldehydes indicate that two competing processes contribute to the overall conversion: a major reaction (reaction mode A) which is responsible for the intramolecular transfer of the aldehydic hydrogen to the α-carbon formerly substituted by the formyl group, and a less important reaction (reaction mode B) which involves a double bond migration and intramolecular transfer of the aldehydic hydrogen to the originally olefinic γ-carbon. Evidence in favor of the occurrence of two such processes was obtained first in the photolysis of type **1** steroidal aldehydes (Chart I).[4b]



$$\overset{\mathrm{HCO}}{\mathrm{C}_\alpha}\!-\!\mathrm{C}\!=\!\mathrm{C}_\gamma \xrightarrow{-\mathrm{CO}} \overset{\mathrm{H}}{\mathrm{C}_\alpha}\!-\!\mathrm{C}\!=\!\mathrm{C}_\gamma \qquad \text{(A)}$$

$$\overset{\mathrm{HCO}}{\mathrm{C}_\alpha}\!-\!\mathrm{C}\!=\!\mathrm{C}_\gamma \xrightarrow{-\mathrm{CO}} \mathrm{C}_\alpha\!=\!\mathrm{C}\!-\!\overset{\mathrm{H}}{\mathrm{C}_\gamma} \qquad \text{(B)}$$

The decarbonylation of laurolenal (**8**) with hydrogen transfer according to reaction mode B at wavelengths >3000 Å (main absorption at 3130 Å) was shown, using the trideuteriomethyl-labeled aldehyde **8**-d_3 (→ 11.3% **31**), to approximate closely the extent of both half of the loss of optical activity in the decarbonylation of (+)-**8** (*i.e.*, → 12% (+)-**29**) and the maximum incorporation (*ca.* 9%) of hydrogen from tri-*n*-butylstannane (Charts IV and VIII). The correspondence of these values suggests that the formation of (−)- and (+)-hydrocarbons **29** from (+)-**8** is mainly due to the stereospecific reaction modes A and B, respectively. An alternative possibility was that a process of random hydrogen addition to a trimethylcyclopentenyl radical intermediate competing with the major reaction A accounted for the observed partial racemization. However, both the close agreement between optical result of the decarbonylation of (+)-**8** and product ratio **30**/**31** from **8**-d_3 and the absence of any scrambling

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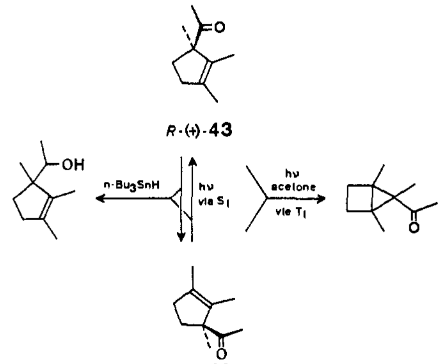
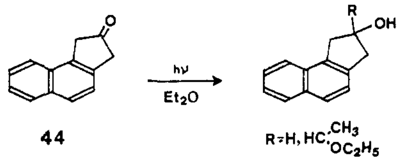
(34) *Cf.* J. Ipaktschi, *Tetrahedron Lett.*, 2153 (1969), and references therein.

(35) (a) E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969); (b) H. Gonzenbach, M. J. Jorgenson, and K. Schaffner, unpublished results. In contrast to the photochemical behavior of aldehyde 8, the most efficient unimolecular process of singlet excited methyl ketone **43** is a sigmatropic 1,3-acyl shift. α cleavage and radical dissociation are less important in this case.



(36) Decarbonylation of 8 is the only photochemical reaction observed also in the presence of *trans*-1,2-dicyanoethylene. The formation of oxetane adducts with this olefin has been shown for singlet excited aliphatic and cyclic ketones: N. J. Turro, P. A. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *J. Amer. Chem. Soc.*, 89, 3950 (1967); N. J. Turro, P. A. Wriede, and J. C. Dalton, *ibid.*, 90, 3274 (1968).

(37) Other examples of reductions of singlet excited carbonyl compounds, all of which possess β unsaturation, have been found since.



44

They include α-aryl aldehydes[32] and methyl ketone **43**[35a] with stannane, and benz[*e*]indan-2-one (**44**)[38] with ether as the hydrogen donors.

(38) A. Tuinman, Doctoral Dissertation, ETH Zürich, 1969.

(39) (a) G. S. Hammond and P. A. Leermakers, *J. Amer. Chem. Soc.*, 84, 207 (1962); (b) P. J. Wagner, *ibid.*, 89, 2503 (1967); (c) P. Keller, G. Eggart, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 50, 2259 (1967); (d) K. Schaffner, *Pure Appl. Chem.*, 16, 75 (1968).

(40) The quantum yield for reduction (φ_{red}) of **8** with 0.34 *M* stannane, resulting in a 1:1.3 ratio of decarbonylation and reduction, can be estimated to equal *ca.* 0.44, assuming a primary quantum yield of α cleavage equal to 1 with $\Phi_{-\mathrm{CO}}$ (decarbonylation) = 0.61 and ϕ_{rec} (recombination) = 0.39 in the absence of stannane, and hence (dashes denote quantum yields in the presence of stannane)

$$\phi_{-\mathrm{CO}}' + \phi_{\mathrm{rec}}' + \varphi_{\mathrm{red}} = 1.0$$

$$\varphi_{\mathrm{red}} = 1.3\phi_{-\mathrm{CO}}'$$

$$\phi_{-\mathrm{CO}}'/\phi_{\mathrm{rec}}' = \phi_{-\mathrm{CO}}/\phi_{\mathrm{rec}} = 0.61/0.39$$

The expression for k_{red} derives from the equation

$$\varphi_{\mathrm{red}} = (k_{\mathrm{red}}[\mathrm{Bu_3SnH}])/(k_{\mathrm{red}}[\mathrm{Bu_3SnH}] + k_{\alpha})$$

of deuterium labels in the mixed experiment with **8**-d_1 + **8**-d_3 serve to discard this possibility. The limitation of hydrogen incorporation from stannane to *ca.* 9% at high donor concentrations and >3000 Å suggests, furthermore, that participation of the external hydrogen source is restricted to process B. This was confirmed unequivocally in the case of aldehyde **9**-d_1. Here the products of paths A and B, unlike the enantiomeric forms resulting from the isomeric aldehyde **8** with an endocyclic double bond, differ in their constitutions and are isolable. The introduction of external hydrogen was observed exclusively in the product of reaction mode B, trimethylcyclopentene **39**, whereas the initial deuterium label remained intact in the methylenedimethylcyclopentane **38**-d_1 resulting from process A (Chart VIII).

Reaction mode A has formal precedent in the results of vapor phase photolyses of acetaldehyde. Parmenter and Noyes[41] have shown that at 3340-Å photochemical energy dissipation from excited gaseous acetaldehyde is mainly α cleavage to radicals (reaction 1) from the triplet state. Dissociation from vibrationally excited singlet state molecules to form directly molecular products, methane and carbon monoxide (reaction 2), occurs simultaneously and with increasing relative importance at shorter wavelengths.[42] As a tentative

$$CH_3CHO + h\nu \longrightarrow CH_3\cdot + \cdot CHO \qquad (1)$$

$$\longrightarrow CH_4 + CO \qquad (2)$$

mechanistic explanation for this latter process the authors[41] proposed an insertion of the aldehydic hydrogen between the two carbon atoms by a combination of carbon–carbon stretching and carbon–hydrogen bending motions. One objection may be raised immediately, however, against a more than merely superficial analogy with reaction mode A of the β,γ-unsaturated aldehydes. The photodecarbonylation in solution will be preceded almost certainly by rapid collisional deactivation of vibrational excitation, and consequently reaction is expected to occur from the thermally equilibrated electronic state. In accordance with this expectation, reactions A and B are observed with excitation wavelength 3341 Å which is near the long-wavelength origin of the first absorption band (**8**, *ca.* 3500 Å in isooctane, see Figure 1). Irradiation with shorter wavelengths does not increase the reaction efficiency, but rather tends to decrease somewhat the quantum yield (Table II) (*vide infra* for the discussion of the wavelength dependencies of the reactions A and B of *R*-(+)-**8** and of the incorporation of stannane hydrogen in the photolysis of **8**-d_1).

The small isotope effect of *ca.* 1.1 observed for the decarbonylation of the aldehydes **8** and **8**-d_1 may constitute further evidence against a direct rearrangement of hydrogen in reaction A involving a vibrationally excited state. Although the observed value is in the order of secondary isotope effects in thermal reactions, we are not aware, however, of a firm basis for evaluating the magnitude of a primary effect in such an electronically excited state process at this stage of the investigation. *The possibility remains, then, that reaction A represents a concerted elimination process from the equilibrated excited singlet state, an allowed process according to orbital symmetry conservation rules.*[43a]

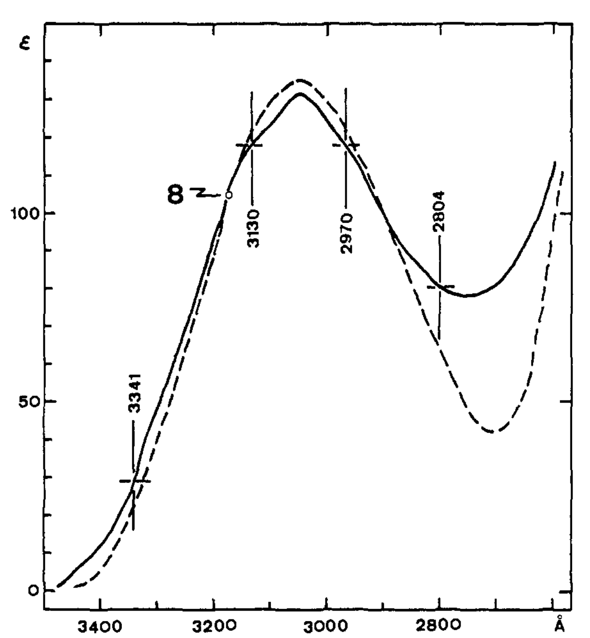


Figure 1. n → π* absorptions of aldehyde **8**: ——, in isooctane; — — —, in ethanol.

An alternative mechanism for reaction A is seen in the decay of the singlet excited rotamer B (a homoconjugated conformation for aldehyde *R*-**8**) to an allyl–formyl radical pair E_B (Chart IX). The aldehydic hydrogen is suitably oriented in this intermediate for a selective incorporation at C_α upon liberation of carbon monoxide. The relative orientation of the two radical components in E_B would already be preformed in the excited homoconjugated state which is pictured to dissociate in an α-cleavage process (Norrish type I fission).[43b] A close association would be maintained through the bonding interaction of five electrons delocalizing over five centers (with a σ type orbital overlap between the allyl and the formyl radicals).

Conformation C corresponds to the orientation of strongly homoconjugated cyclic β,γ-unsaturated ketones,[7,9] and it should therefore show appreciably enhanced and red-shifted n → π* absorption as well. The third contributor to the rotamer composition, D, is presumably[9] less favorable for homoconjugation. Consequently, excitation of D should be negligible at long wavelengths ($\gtrsim$3130 Å), but participate increasingly at decreasing wavelengths. The orientations of the formyl and allyl radicals resulting from α cleavage of the excited rotamers C and D provide for a less intimate association in the *incipient* radical pairs E_C and E_D than in E_B. While the hydrogen in E_C and E_D is still favorably placed for reaction A, *i.e.*, the addition to C_α (→ *S*-(−)-**29**), the p orbital on C_γ of E_C is now also sufficiently close to the aldehydic hydrogen to permit its transfer to the γ position as well (→ *R*-(+)-**29**). This latter hydrogen transfer process can account then for reaction B of aldehyde *R*-(+)-**8**.

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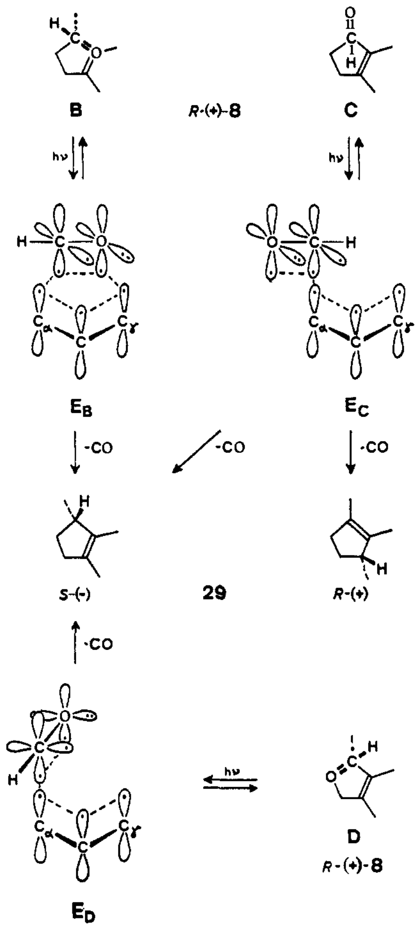
[41] C. S. Parmenter and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **85**, 416 (1963).

[42] 3130 Å, $\varphi_1 \geq 0.20$ and $\varphi_2 \simeq 0.001$; 2804 Å, $\varphi_1 \geq 0.39$ and $\varphi_2 \geq 0.15$; 2537 Å, $\varphi_1 = 0.38$ and $\varphi_2 = 0.66$; see ref 31a, p 371.

[43] (a) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969). (b) See H. E. Zimmerman, *Advan. Photochem.*, 1, 183 (1963), for a discussion of the detailed electronic changes involved in the photolytic α-cleavage process.

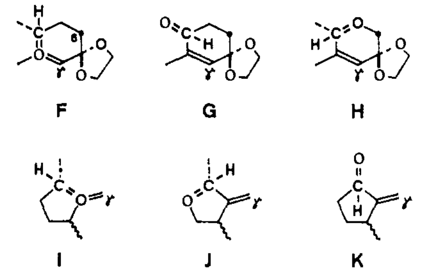
Chart IX. Photodecarbonylation of Aldehyde *R*-(+)-**8**. Mechanism Involving α Cleavage to Allyl–Formyl Radical Pairs



The mechanistic scheme invoking type E radical-pair intermediates[44] for reactions A and B can accommodate satisfactorily the observations (1) that in the photolysis of **8**-d_1 (and of **9**-d_1) at $\gtrsim$3130 Å in the presence of tri-*n*-butylstannane hydrogen incorporation participates selectively at the decarbonylation mode B and (2) that the ratio of reactions A and B of *R*-(+)-**8** and the extent of stannane hydrogen incorporation in the photolysis of **8**-d_1 are wavelength dependent. If the rotamers B and C absorb predominantly in the long-wavelength region and rotamer D in the short-wavelength portion (<3130 Å) of the n → π* band of **8** (Figure 1), reaction B involving hydrogen transfer to C_γ in E_C can be expected to be more important at 3341 than at 2801 Å. Accordingly, racemization of product **29** increases from 2804 to 3341 Å by 6%. The decrease of stannane hydrogen uptake from 21 to 8% upon the same change of excitation wavelengths demands that the allyl components of the radical pairs E_C and E_D incorporate hydrogen from an external source more efficiently than the allyl moiety of the more closely associated form E_B.[45] Furthermore, addition of external hydrogen to E_C and E_D, as a competitive process to the intramolecular hydrogen transfer of reaction B, should occur preferentially at C_γ (and not at C_α).

Extension of this mechanism to the decarbonylation of aldehydes **7** and **9** can lead in each case to a similar situation with respect to the incipient radical pairs, with rotamers F and I, G and J, and H and K (Chart X) furnishing intermediates of type E_B, E_C, and E_D, respectively. However, the substantially greater reactivity toward incorporation of external hydrogen (9% hydrogen from *pentane* in **28**-d_1, the photoproduct of **7**-d_1, and 10% in **39**, one of the two products of **9**-d_1, *vs.* no hydrogen uptake in the photolysis of **8**-d_1 in the same solvent) as well as the absence of reaction mode B in the photolysis of **7** (as indicated by the formation of one product, **28**, only) are deviations from the previous reaction pattern which can be attributed to structural differences between the aldehydes **1**, **7**, **8**, and **9**. The β,γ-unsaturated aldehyde system of the steroid compound **1** and of laurolenal (**8**) differ from those of compounds **7** and **9** with respect to conformational flexibility. The condensed ring system of **1** holds the angular formyl group in a rigidly fixed axial position above the cyclohexenyl ring. The cyclopentenyl ring of **8** provides for a similarly rigid fixation of carbonyl group and double bond. In both aldehydes spatial arrangements capable of a close association of the two radical partners in the incipient type E intermediate are thus preformed. The greater flexibility of compounds **7** and **9**, however, allows the formyl substituent to adopt also conformations (equatorial and pseudoequatorial) in which the relative orientations of the two groups are less suitable for pair formation. As a consequence, the tendency toward radical dissociation will increase and hydrogen abstraction from the solvent become important enough to account for the observed incorporation from pentane in the photolyses of **7**-d_1 and **9**-d_1. The selective addition of hydrogen to the primary carbon-2′ of the allyl radical **46** and to the tertiary carbon-4 of **47** could well reflect the combined effects of the greater

Chart X. Rotamers of Aldehydes 7 and 9



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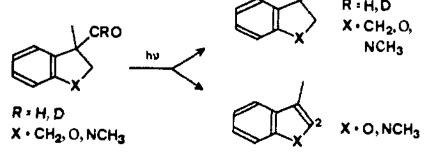
[44] Preliminary results with the aromatic aldehyde series **45** provide independent indications for the intermediacy of radical pairs (*cf.* E) in



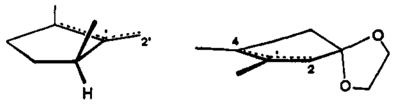
45

the photodecarbonylation. While 1-formyl-1-methylindan (48, X = CH_2) decarbonylates uniformly to methylindan in close analogy to laurolenal (8), the heterocyclic aldehydes (X = O and NCH_3), which are capable of both stabilizing type E radical pairs and facilitating radical removal of hydrogen from position C-2, exhibit competitive decomposition to the correspondig Δ^2-unsaturated compounds in addition to decarbonylation (Diploma Theses, ETH Zürich, of K. Müller (1967) and H. Gonzenbach (1968); H. Wolf, unpublished results).

[45] The proposed reaction scheme (Chart IX) requires that the hydrogen transfer within the radical pairs E_{B-D} and the incorporation of stannane hydrogen to E_C and E_D can compete in rate with the conformational equilibration of the three incipient rotameric intermediates.

reactivity difference between the terminal allyl radical positions in **46** (primary *vs.* tertiary) than in **47** (secondary *vs.* tertiary), and a greater steric shielding of C-2 in **47** than of C-2′ in **46**.

Chart XI. Allyl Radicals from Dissociative α Cleavage of Aldehydes 7 and 9



46 **47**

The failure of aldehyde **7** to undergo reaction B indicates, within this mechanistic framework, that the contribution by rotamer G is negligible. A model inspection of the rotational barriers imposed on the formyl substituent of **7** shows that in the chair form rotamer G exhibits a nonbonding interaction between the hydrogens in the axial C-6 position and on the formyl carbon (and in rotamer H between CH-6 and the carbonyl oxygen), whereas conformation F is free of such hindrance. Rotamer F should therefore be sterically more favorable than G. Moreover, it appears plausible that, in accordance with the respective photochemical results concerning reaction B, preference for F over G in **7** should be greater than the preference for A in the steroid **1** over a G-like conformer, as the difference in steric interactions in the rotamers of **1** appears smaller[10] than in **7**.

Decarbonylation Quantum Efficiency of Aldehydes 7 and 8. The quantum yields of decarbonylation for **7** and **8** are somewhat dependent on both the solvent nature and the excitation wavelength except for the irradiations in *t*-butyl alcohol where the quantum yields for each compound were the same at 2970 and 3130 Å (Table II). It has already been pointed out that the quantum efficiency of the photochemical α cleavage may be close to unity, and that the observed average value of *ca.* 0.5 for $\phi_{-\mathrm{CO}}$ of **7** and **8** may reflect the competition between the reversal of the primary photoprocess and the secondary decarbonylation step. Solvent effects on the quantum yields of decarbonylation at a given wavelength may therefore originate from the solvent effects on the reactivity of the radical pair intermediate (and, possibly, on the rotamer composition). The lower quantum yields in hexane and in benzene at the shorter wavelength, 2970 Å, are readily understood if it is assumed that at this wavelength the nonhomoconjugated rotamers (*cf.* D and H) participate at the light absorption to a greater extent than at 3130 Å, and that they exhibit a lower quantum yield of decarbonylation than the conjugated conformers. The difference in $\phi_{-\mathrm{CO}}$ between 2970 and 3130 Å will necessarily become smaller, and in fact is zero, upon irradiation in *t*-butyl alcohol as in this solvent the n → π* absorptions of the nonconjugated rotamers will be blue shifted relative to the absorptions in hexane and benzene, whereas the n → π* bands of the conjugated forms remain largely insensitive to the change in solvents.

Photochemistry of Aldehyde 10. Photochemical Reduction and Formation of Aliphatic Ketones. Compound **10** is a bridged structural analog of aldehyde **9**. The formal ring closure between the two methyl groups forces the CO–C$_\alpha$ σ bond and the double bond into the same plane and thus provides for **10** a conformation which **9** will not adopt to any appreciable extent. It is unfavorable for homoconjugation and, moreover, prevents facilitation of photochemical α cleavage by the allylic π system of the double bond. These factors are seemingly determinant for the photochemical behavior of **10**, *i.e.*, it shows no tendency toward decarbonylation, but rather preference for singlet–triplet intersystem crossing and reactions from the triplet state. The photoreduction of **10** to alcohol **27** in isopropyl alcohol and in pentane, subject to quenching by naphthalene, is characteristic of triplet excited aldehydes and ketones.

Competition in the poorer hydrogen donor pentane by the formation of methyl and ethyl ketones **40** and **41** is without precedent. No experimental evidence concerning the mechanism of this novel photoreaction of an aldehyde is available yet. It would seem plausible, however, that in these ketone formations acyl radicals are generated from excited aldehyde, capable of intercepting radicals which form upon hydrogen abstraction by excited aldehyde from the solvent. Photochemical Norrish type II breakdown of the resulting 1-, 2-, and 3-pentanyl ketones would ultimately lead to **40** and **41**. For the primary photochemical process of acyl radical formation two alternatives appear possible: either the photolytic elimination of the aldehydic hydrogen,[46] or abstraction of this hydrogen from a ground-state aldehyde by an excited counterpart.

Experimental Section[47]

Methyl (±)-3-Methylcyclohex-3-en-1-one-4-carboxylate Ethylene Ketal (12). A mixture of 19.56 g (0.117 mol) of Hagemann's ester (**11**),[12] 200 mg of *p*-toluenesulfonic acid, and 20 ml of ethylene glycol in 200 ml of benzene was refluxed with stirring using a water separator for 6.5 hr. The cooled mixture was poured onto water and the benzene layer washed with 2% sodium bicarbonate solution and with water. The benzene was removed *in vacuo* and the residue distilled. The product (20.07 g, 85% yield) distilled at 124–125° (2 mm): ir (film) 1072, 1098, 1250, 1640, and 1710 cm^{-1}; nmr (CCl$_4$) δ 1.98 (s with fine splitting, 3 H), 3.65 (s, 3 H), 3.87 (s, 4 H).

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[46] The reaction RCHO + *hν* → RCO· + ·H has been observed to date in flash photolyses only [M. A. Kahn, R. G. W. Norrish, and G. Porter, *Proc. Roy. Soc., Ser. A*, **219**, 312 (1953)], and similar observations in conventional solution photochemistry have not been reported.

[47] Vpc were run on Varian-Aerograph A-90-P3 models, using helium and the following columns: 15% Carbowax 20M on Chromosorb P (80–100 mesh) (20M/P), 20% Carbowax 20M on Chromosorb W (60–80 mesh) (20M/W), 20% silicone fluid SF-96 on Chromosorb W (60–80 mesh) (SF-96), 20% silicone gum rubber on Chromosorb W (60–80 mesh) (SE-30 and SE-52), 15% UCON nonpolar 1715 on Chromosorb W (60–80 mesh) (UCON), 20% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P (45–60 mesh) (TCEP). Melting points were determined in open capillaries and are not corrected. Optical rotations were obtained on a Zeiss polarimeter 0.005°, using a 5-cm polarimeter tube unless specified otherwise. Ir and uv spectra were measured on Perkin-Elmer Model 257 and 137 spectrophotometers, respectively. Nmr spectra were obtained from dilute solutions with tetramethylsilane as internal standard using Varian spectrometers operating at 60 and 100 Mcps (Models A-60A and HA-100, respectively). First-order multiplets in nmr spectra are described by use of abbreviations s for singlet, d for doublet, t for triplet, q for quartet; m is used for multiplets not described by other symbols. Mass spectra were measured on Hitachi-Perkin-Elmer RMU-6a and RMU-6D spectrometers. Microanalyses were carried out by Mr. W. Manser of the Microanalytical Laboratory, ETH. 80-W (Q81, Quarzlampen GmbH., Hanau) and 125-W medium-pressure (Meda Licht AG., Basel), and NK6/20 low-pressure mercury lamps (Quarzlampen GmbH.) were used as the light sources for the uv irradiations. Light filters included Pyrex (cut-off at *ca.* 2900–3000 A) and acetone (1.5-cm path, cut-off at *ca.* 3270 Å). The merry-go-round reactor[48] was equipped with a 125-W lamp in a double Pyrex jacket. The inner jacket was water cooled, and the outer jacket contained, if required, the filter solution. Each sample tube was stirred magnetically during the photolysis. Degassing involved three freeze–thaw cycles at 10^{-5} mm, and subsequent sealing of the evacuated tube.

[48] *Cf.* F. G. Moses, R. S. H. Liu, and B. M. Moore, *Mol. Photochem.*, **1**, 245 (1969).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.79; H, 7.80.

(±)-3-Methyl-4-hydroxymethylcyclohex-3-en-1-one Ethylene Ketal (13). Ester **12** (74.35 g, 0.347 mol) was added to 27 g of lithium aluminum hydride in 1.2 l. of anhydrous ether. The mixture was stirred overnight at room temperature and excess hydride decomposed by the addition of moist ether followed by approximately 25 ml of water. The inorganic precipitate was removed by vacuum filtration and washed thoroughly with 1 l. of ether. The combined filtrates were concentrated *in vacuo* and diluted with 500 ml of benzene, and the solvent removed *in vacuo*. Distillation of the residue gave 62.12 g (91% yield) of pure product: bp 126–127° (1 mm), 95° (0.1 mm); ir (film) 1020, 1062, 1092, and 3300 cm^{-1}; nmr (CCl_4) δ 1.66 (s with fine splitting, 3 H), 3.88 (s, 4 H), 4.01 (broad "s", 2 H).

(±)-3-Methyl-4-hydroxymethylcyclohex-3-en-1-one-4′-d_2 Ethylene Ketal (13-d_2). The procedure described above for the preparation of alcohol **13** was employed, but using lithium aluminum deuteride. Distillation of the crude product gave 88% yield of pure compound: bp 152–155° (8 mm); ir (film) 1060, 1090, 2200, 2085, and 3350 cm^{-1}; mass spectrum, 95% d_2.[5,49]

(±)-3-Methyl-4-formylcyclohex-3-en-1-one Ethylene Ketal (14). An ice-cooled flask containing 130 ml of dry pyridine was treated portionwise with 11 g of chromic oxide. The cooling bath was removed and 6.21 g (31.7 mmol) of alcohol **13** in 40 ml of dry pyridine was added in rapid drops. The resulting mixture was stirred for 16 hr, then diluted with 100 ml of benzene, and stirred for 1 hr. After filtration and washing of the inorganic precipitate with 200 ml of benzene, the combined filtrates were concentrated *in vacuo*, dissolved in 20 ml of benzene, and filtered over 30 g of neutral alumina, activity IV, to remove suspended inorganic material. The alumina was washed with 100 ml of benzene and the combined filtrates were concentrated *in vacuo*. Distillation of the residue at 0.1 mm (bp 86°) yielded 5.85 g (95% yield) of pure aldehyde **14**: uv (EtOH) max 247 mμ (ϵ 16,000); ir (film) 1062, 1087, 1620, 1664, 2780 cm^{-1}; nmr (CCl_4) δ 2.12 (broad "s," 3 H), 3.92 (s, 4 H), 10.05 (s, 1 H).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.72; H, 7.70.

(±)-3-Methyl-4-formylcyclohex-3-en-1-one-4′-d_1 Ethylene Ketal (14-d_1). The procedure described above for the preparation of aldehyde **14** was employed, but using alcohol **13**-d_2. Distillation of the crude product at 12 mm (bp 158–162°) gave 80% yield of pure product: ir (film) 1064, 1094, 1639, 1653, 2160 cm^{-1}; mass spectrum, 97% d_1.[5,49]

(±)-3,4-Dimethyl-4-formylcyclohex-2-en-1-one Ethylene Ketal (7). A solution of 78 g (0.557 mol) of methyl iodide in 1 l. of dry *t*-butyl alcohol containing 57.0 g (0.313 mol) of aldehyde **14** was added dropwise at 23° to a solution of 36 g (0.32 mol) of potassium *t*-butoxide in 250 ml of *t*-butyl alcohol. After stirring overnight with nitrogen bubbling through the mixture throughout the entire addition and reaction period of 16 hr, the solvent was removed under reduced pressure. The residue was treated with benzene and water. Concentration of the organic phase *in vacuo* and distillation of the residue at 0.1 mm (bp 78°) yielded 35.35 g (58% yield) of pure aldehyde **7**: uv, see Table I; ir (film) 1078, 1670, 1705, 2700 cm^{-1}; nmr (CCl_4) δ 1.15 (s, 3 H), 1.65 (d, J = 1 cps, 3 H), 3.90 (s, 4 H), 5.50 (s with fine splitting, 1 H), 9.42 (s, 1 H); mass spectrum, *m/e* 196 (M^+).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.30; H, 8.21.

(±)-3,4-Dimethyl-4-formylcyclohex-2-en-1-one-4′-d_1 Ethylene Ketal (7-d_1). The procedure described above for the preparation of aldehyde **7** was employed, but using aldehyde **14**-d_1 as the starting material. Distillation of the crude product at 2 mm (bp 112–115°) gave pure aldehyde **7**-d_1 in 73% yield; ir (film) 1087, 1661, 1709, 2045, 2120 (shoulder) cm^{-1}; mass spectrum, 97% d_1.[5,49]

Irradiation of Aldehydes 7 and 7-d_1. (a) A solution of 1.80 g (9.2 mmol) of aldehyde **7** in 110 ml of dry pentane was irradiated in a cylindrical reactor equipped with a central 80-W lamp in a water-cooled Pyrex jacket. Stirring was effected with a nitrogen stream introduced through an inlet at the bottom. After 6 hr the reaction was completed with no substantial products other than decarbonylated material **28** (vpc on SF-96 at 165°). The solvent was removed giving 1.520 g (93% yield) of **3,4-dimethylcyclohex-2-en-1-one ethylene ketal (28).** Samples for analytical purposes were purified by vpc: ir (film) 1134, 1670 cm^{-1}; nmr (CS_2) δ 1.01 (d, J = 7 cps, 3 H), 1.67 (d, J = 1.5 cps, 3 H), 3.80 (s, 4 H), 5.19 (finely split m, 1 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.28; H, 9.65.

Ketal **28** (247 mg (1.4 mmol)) was dissolved in 25 ml of ether, treated with 0.5 ml of 6 *N* aqueous hydrochloric acid, and stirred at room temperature for 15 min. The mixture was dried with anhydrous potassium carbonate and filtered and the filtrate concentrated at reduced pressure leaving 159 mg (92% yield) of **3,4-dimethylcyclohex-2-en-1-one** which was purified by vpc for analysis: uv (EtOH) max 235 (ϵ 11,100), 309 mμ (ϵ 33); ir ($CHCl_3$) 1634, 1667 cm^{-1}; nmr ($CDCl_3$) δ 1.21 (d, J = 6 cps, 3 H), 1.96 (d, J = 1.5 cps, 3 H), 5.83 (finely split m, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.20; H, 9.83.

A solution of 336 mg (2 mmol) of ketal **28** in 10 ml of methanol was treated with 2 drops of 6 *N* aqueous hydrochloric acid and stirred for 15 min at room temperature. Semicarbazide hydrochloride (300 mg) was then added, and the mixture was neutralized with 3 *N* aqueous sodium hydroxide. Upon chilling 158 mg (44% yield) of crystals precipitated. Recrystallization yielded **3,4-dimethylcyclohex-2-en-1-one semicarbazone** of mp 181–182° (lit.[19] 182–183°).

(b) A 2% solution of aldehyde **7** in *t*-butyl alcohol was irradiated for 1.5 hr in the reactor described in (a). Vpc indicated that the aldehyde was completely decarbonylated to **28**.

(c) A 0.6% solution of aldehyde **7** in neat 1,3-pentadiene was irradiated as in (a). After 2 hr the aldehyde had been converted completely to **28** (vpc).

(d) A 0.2% solution of aldehyde **7** in benzene was irradiated in the reactor as described in (a), but equipped with a low-pressure lamp (main emission at 2537 Å) in a quartz jacket for a maximum of 16 hr. No decarbonylation could be detected by vpc after this period.

(e) Solutions (1%) of aldehyde **7**-d_1 (97% d_1) in pentane and in pentane containing 4% tri-*n*-butylstannane, respectively, were irradiated in the reactor described in (a). After 50% conversions of aldehyde the solutions were concentrated under reduced pressure, and the photoproducts (**28**-d_1) were isolated by vpc.[49] The sample of **3,4-dimethylcyclohex-2-en-1-one-4-d_1 ethylene ketal (28-d_1)** obtained from the run in neat pentane [nmr (CS_2) δ 1.01 (mostly s, 3 H), 1.67 (d, J = 1.5 cps, 3 H), 3.80 (s, 4 H), 5.19 (finely split m, 1 H)] contained 88% d_1, and the sample from the run in pentane + stannane 77% d_1.[5]

(*R*)-(+)-Laurolenic acid (15) was prepared from (−)-α-bromocamphoric anhydride[50] by the procedure described by Meyer, *et al.*:[13] $n^{23}\text{D}$ 1.4782; d^{23} 1.023; pK_a = 7.90 (in methyl Cellosolve–water 4:1); $[\alpha]^{23}\text{D}$ +185.4 ± 1.1° (liquid), $[\alpha]^{24}\text{D}$ +155.9 ± 1.6° (*c* 2.2, $CHCl_3$) [lit.[13] $n^{27}\text{D}$ 1.4740, $[\alpha]^{23}\text{D}$ +155° (*c* 0.64, $CHCl_3$)].[51]

Methyl (*R*)-(+)-laurolenoate (16) was obtained from **15** with diazomethane:[13] bp 75–76° (14–15 mm); $n^{23}\text{D}$ 1.4570; d^{23} 0.972; $[\alpha]^{23}\text{D}$ +154° (liquid), $[\alpha]^{24}\text{D}$ +132° (*c* 1.8, $CHCl_3$]; ir (liquid) 1105, 1160, 1725, 2840 cm^{-1}; nmr ($CDCl_3$) δ 1.25 (s, 3 H), 1.55 and 1.65 (two broad "s," 3 H each, with long-range coupling to other allylic protons), 3.65 (s, 3 H); mass spectrum, *m/e* 168 (M^+), 109 ($M^+ - COOCH_3$, base peak).[51]

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.44; H, 9.31.

The **cyclohexylammonium** salt was prepared from 6.15 g (40 mmol) of acid **16** and 4.1 g (41.2 mmol) of freshly distilled cyclohexylamine which were slowly warmed to 50° in 50 ml of ethyl acetate with continuous stirring. On cooling, 8 g of crystals precipitated. Two crystallizations from ethyl acetate afforded 7.2 g (71% yield) of mp 114° which was sublimed at 100° (0.1 mm): $[\alpha]^{22}{}_{546}$ + 112.9 ± 0.9° (*c* 2.0, $CHCl_3$); ir (KBr) 1380, 1520, 1630, 2000–3500 (broad) cm^{-1}.[51]

Anal. Calcd for $C_{15}H_{27}NO_2$: C, 71.10; H, 10.74; N, 5.53. Found: C, 71.10; H, 10.78; N, 5.54.

(*R*)-Laurolenoyl Chloride (17). Acid **16** (1.5 g (9.7 mmol)) in 10 ml of anhydrous ether was added dropwise and with vigorous stirring to a solution of 16.55 g (139 mmol) of thionyl chloride and *ca.* 4 drops of pyridine in 20 ml of anhydrous ether. After refluxing

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(49) In vpc the compounds 7-d_1, **13**-d_2, **14**-d_1, 28-d_1 (on SF-96 at temperatures varying from 140 to 180°), 8-d_1 8-d_3, **9**-d_1, 18-d_1, 18-d_2, **18**-d_3, 20-d_3, 22-d_3, **24**-d_2, **29**-d_1, **30**, **31**, **36**, and **37** (on UCON at 100–180°) were indistinguishable from the appropriate nondeuterated analogs.

(50) O. Aschan, *Ber.*, 27, 2112, 3504 (1894); *Ann.*, 290, 185 (1896).

(51) For the circular dichroitic data of compounds **15**, **16**, the cyclohexylammonium salt, and the cyclohexylamide of **16**, see ref 10.

for 2 hr, pyridine hydrochloride was filtered off and the ether and excess thionyl chloride were removed by fractionated distillation at reduced pressure. Vacuum distillation of the residue afforded 1.34 g (80% yield) of pure acid chloride **17**: bp 72–73° (10 mm); ir (film) 1784 cm^{-1}; nmr (CCl_4) δ 1.33 (s 3 H), 1.58 and 1.66 (two broad "s," 3 H each).

Anal. Calcd for $C_9H_{13}OCl$: C, 62.60; H, 7.59; Cl, 20.54. Found: C, 62.43; H, 7.80; Cl, 20.40.

The acid chloride **17** was further characterized as the **cyclohexylamide derivative:** 1 g (5.8 mmol) of acid chloride **17** was dissolved in 20 ml of anhydrous dioxane, and 4 g (40 mmol) of cyclohexylamine in 20 ml of dioxane was added dropwise at room temperature with stirring. After 0.5 hr 150 ml of ice water was added. On acidification, the amide precipitated. Crystallization from methanol–water gave 1.25 g (92% yield) of mp 64.5–65°; $[\alpha]^{24}{}_{546}$ + 69° (*c* 3.1, EtOH), $[\alpha]^{24}{}_{D}$ +56° (*c* 3.7, EtOH); ir ($CHCl_3$) 1500, 1650, 2995, 3400, 3450 cm^{-1}; nmr ($CDCl_3$) δ 1.22 (s, 3 H), 1.55 and 1.70 (two broad "s," 3 H each).[51]

Anal. Calcd for $C_{15}H_{25}NO$: C, 76.54; H, 10.71; N, 5.95. Found: C, 76.52; H, 10.88; N, 5.83.

(*R*)-(+)-Laurolenol (18). Acid **15** (1 g (6.5 mmol)) in 30 ml of anhydrous ether was added dropwise to 250 mg (6.6 mmol) of lithium aluminum hydride in 50 ml of ether at room temperature with stirring. The reaction mixture was refluxed subsequently for 1 hr, then 50 ml of a 2 *M* solution of Seignette salt was added slowly. Extraction with ether gave 840 mg (93% yield) of a colorless oil: bp 79–80° (10 mm); $n^{23}{}_{D}$ 1.4762; d^{23} 0.927; $[\alpha]^{23}{}_{D}$ +27° (neat), $[\alpha]^{23}{}_{D}$ +16° (*c* 3.2, $CHCl_3$); ir ($CHCl_3$) 1035, 1045, 3400 cm^{-1}; nmr ($CDCl_3$) δ 0.97 (s, 3 H), 1.50 and 1.65 (two broad "s," 3 H each), 3.28 and 3.47 (two d, J = 10 cps, 1 H each); mass spectrum, *m/e* 140 (M^+), 109 ($M^+ - CH_2OH$, base peak).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.91; H, 11.65.

(*R*)-(+)-Laurolenol-1′-d_2 (18-d_2). The procedure as described above for the preparation of alcohol **18**, but using lithium aluminum deuteride, was employed: ir ($CHCl_3$) 1060, 2080, 2200, 3350 cm^{-1}; mass spectrum, 100% d_2.[5,49]

(*R*)-(+)-Laurolenol (18) 3,5-Dinitrobenzoate. Alcohol **18** (560 mg (4 mmol)) in 5 ml of pyridine was added dropwise at room temperature to a solution of 1 g (4.26 mmol) of 3,5-dinitrobenzoyl chloride in 10 ml of pyridine. After stirring overnight and the usual work-up 1.34 g of yellow crystals was obtained. Two crystallizations from methanol–water gave 1.04 g (78% yield) of mp 94°: $[\alpha]^{22}{}_{D}$ +24° (*c* 1.7, $CHCl_3$); uv (EtOH) max 230 mμ (ϵ 187,500); ir ($CHCl_3$) 920, 970, 985, 1075, 1270, 1550, 1630, 1730, 3095 cm^{-1}.

Anal. Calcd for $C_{16}H_{18}N_2O_6$: C, 57.48; H, 5.43. Found: C, 57.40; H, 5.53.

(*R*)-(+)-Laurolenal (8). The procedure of Doering, *et al.*,[14] was employed. Alcohol **18** (1 g, 7.15 mmol) was dissolved in 20 ml of freshly distilled dimethyl sulfoxide and 5 g (49.5 mmol) of triethylamine. A solution of 3.5 g (22 mmol) of sulfur trioxide–pyridine complex[52] in 20 ml of dimethyl sulfoxide was added dropwise within 5 min to the stirred mixture. Stirring was continued for another 30 min at room temperature in the dark, then 100 ml of ice–water was added. The ether extract was thoroughly washed with water and dried over magnesium sulfate, and the solvent removed by distillation from a water bath at 60°. Two consecutive distillations of the residue at 10 mm (bp 59–60°) gave 810 mg (82% yield) of a colorless oil: $n^{23}{}_{D}$ 1.4682; d^{23} 0.867; $[\alpha]^{23}{}_{D}$ +597.0 ± 5.8° (*c* 1.5, $CHCl_3$); uv and circular dichroism, see Table I; ir ($CHCl_3$) 1725, 2690, 2800 cm^{-1}; nmr ($CDCl_3$) δ 1.09 (s, 3 H), 1.45 and 1.70 (two broad "s," 3 H), 9.30 (s, 1 H); mass spectrum, *m/e* 138 (M^+), 109 ($M^+ - CHO$, base peak).

2,4-Dinitrophenylhydrazone of 8 had mp 128–129°. *Anal.* Calcd for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70. Found: C, 56.84; H, 5.90.

(*R*)-(+)-Laurolenal-1′-d_1 (8-d_1). The procedure as described above for the preparation of aldehyde **8**, but starting from alcohol **18**-d_2, was employed: uv (EtOH) 305 mμ (ϵ 138); ir ($CHCl_3$) 1660, 1710, 2040, 2110 cm^{-1}; mass spectrum, 100% d_1.[5,49]

Determination of the Enantiomeric Purity of Aldehyde (+)-8 Used in the Photolyses. (a) A solution of 3.50 g (0.012 mol) of testosterone in 5 ml of pyridine and 30 ml of anhydrous benzene was stirred at *ca.* 5° while 1.73 g (0.01 mol) of laurolenoyl chloride (**17**) was added dropwise. The resulting mixture was refluxed overnight and then poured onto 1 *N* hydrochloric acid. After washing with water, the benzene phase was dried over magnesium sulfate and concentrated by distillation at normal pressure. The viscous residue was chromatographed on 200 g of silica gel Merck, 0.2–0.05 mm, using petroleum ether (bp 30–60°)–ether, 1:2. Crystallization of the main fraction from methanol–water gave 3.6 g (85% yield) of ester, mp 101–102°. Resolution of the diastereoisomeric mixture was accomplished by five further crystallizations when a constant mp of 108.5° was reached (2.05 g): $[\alpha]^{23}{}_{D}$ +171.8 ± 1.8° (*c* 1.9, $CHCl_3$); ir ($CHCl_3$) 1174, 1667, 1710 cm^{-1}.

Anal. Calcd for $C_{28}H_{40}O_3$: C, 79.20; H, 9.50. Found: C, 79.04; H, 9.37.

The resolved ester was reduced with lithium aluminum hydride in boiling anhydrous ether. Chromatography of the crude reaction mixture on silica gel Merck, 0.2–0.05 mm, using petroleum ether–ether gave a laurolenol (**18**) which was further purified by distillation (302 mg, 44.5 % yield) and subsequently oxidized to laurolenal (**8**) as described above. The aldehyde sample had a specific rotation of $[\alpha]^{23}{}_{D}$ +624.2 ± 4.7° (*c* 1.5, $CHCl_3$).

(b) For the isotope dilution analysis laurolenol (**18**) of $[\alpha]^{23}{}_{365}$ +9.88 ± 0.05° (neat),[53] obtained from laurolenic acid (**15**) of $[\alpha]^{23}{}_{D}$ +185.4 ± 1.1° (neat), and (±)-laurolenol-1″,1″,1″-d_3 (**18**-d_3) were used. A mixture of 2.8777 g of **18** and 1.2827 g of **18**-d_3, $[\alpha]^{23}{}_{365}$ +6.83 ± 0.05° (neat),[53] isotope content 30.8 ± 0.5% d_3 (mass spectrometric analysis), was converted into the 3,5-dinitrobenzoate (98% yield, mp 92–93°) as described above. The material was crystallized eight times from methanol–water to give 1.834 g of an ester of mp 96.5° which was hydrolyzed with 3 g of potassium hydroxide in 100 ml of boiling methanol–water, 1:1, for 1 hr. The methanol was evaporated at reduced pressure. Extraction of the residual mixture with ether and distillation of the neutral product gave 520 mg (67% yield) of a mixture of **18** + **18**-d_3, $[\alpha]^{23}{}_{385}$ +4.97 ± 0.05° (neat),[53] isotope content 34.8 ± 0.5% (mass spectrometric analysis). Using the equation[15]

$$[\alpha_{\mathrm{abs}}] = \sqrt{\frac{[\alpha_1][\alpha_2] - Q[\alpha_2]^2}{1 - Q}}$$

where $Q = A_1/A_2$, A_1, $[\alpha_1]$ = isotope content and specific rotation, respectively, of the initial mixture **18** + **18**-d_3, and A_2, $[\alpha_2]$ = isotope content and specific rotation, respectively, of the mixture after partial racemization, for the absolute specific rotation, and

$$\frac{\Delta[\alpha_{\mathrm{abs}}]}{[\alpha_{\mathrm{abs}}]} = \frac{[\alpha_2]\Delta[\alpha_1] + ([\alpha_1] - 2Q[\alpha_2])\Delta[\alpha_2] + \Delta Q[\alpha_{\mathrm{abs}}]}{2[\alpha_{\mathrm{abs}}]^2(1 - Q)}$$

for the relative error, a value of $[\alpha]^{23}{}_{365}$ +10.26 ± 0.11° can be calculated as the absolute specific rotation of **18**.

The enantiomeric purity of the aldehyde used in the photolyses, $[\alpha]^{23}{}_{D}$ + 597 ± 5.8°, as determined by the two methods, is 95.6 ± 1.7% (method a) and 96.3 ± 1.4 % (method b).

Mixture of Ethyl *cis*- and *trans*-(±)-2-Trideuteriomethyl-5-methylcyclopentan-1-one-2-carboxylates (20-d_3). A dispersion of 3.36 g (70 mmol) of sodium hydride in mineral oil was suspended in 100 ml of anhydrous dioxane. Under vigorous stirring a solution of 12.0 g (70 mmol) of ethyl 5-methylcyclopentan-1-one-2-carboxylate (**19**),[54] bp 61–62° (0.2 mm), $n^{22}{}_{D}$ 1.4454, in 30 ml of absolute dioxane was added dropwise. The mixture was refluxed for 1 hr and then cooled to 5–6°. Trideuteriomethyl iodide (10 g, 69 mmol) was added, and stirring was continued overnight at room temperature, followed by removal of dioxane at reduced pressure, addition of 100 ml of water to the residue, and extraction with ether. The combined extracts were washed with dilute sodium hydroxide solution at 2–5° and with water, dried over magnesium sulfate, and concentrated *in vacuo*. Distillation of the crude product afforded 10.75 g (87% yield) of a pure liquid: bp 55–56° (0.2 mm); $n^{23}{}_{D}$ 1.4422; ir ($CHCl_3$) 1030, 1170, 1260, 1730, 1755, 2225 cm^{-1}; nmr ($CDCl_3$, 60 Mcps) δ 1.13 (d, J = 7 cps, 3 H), 1.23 (t, J = 7 cps, 3 H), 4.15 (q, J = 7 cps, 2 H); mass spectrum, 100% d_3.[5,49,55]

Stereoisomeric Mixture of Ethyl (±)-2-Trideuteriomethyl-1,5-dimethylcyclopentan-1-ol-2-carboxylates (21). A solution of

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(52) J. Houben and Th. Weyl, "Methoden der organischen Chemie," Vol. IX, Georg Thieme Verlag, Stuttgart, 1955, p 506.

(53) Rotations measured in a 1-cm polarimeter tube.

(54) L. Bouveault and R. Locquin, *Bull. Soc. Chim. Fr.*, **3**, **441** (1908); *C. R. Acad. Sci.*, **146**, 138 (1908).

(55) Meyer, *et al.*,[13] report that a mixture of two stereoisomers in nearly equal quantities resulted in a similar preparation of the methyl ester analog of 20. The nmr spectrum of product 20-d_3 also indicates a mixture, but the resolution at 60 Mcps was not sufficient to analyze both sets of signals clearly. The data given correspond to those of the slightly predominant component.

methylmagnesium iodide, prepared from 4.25 g (27 mmol) of methyl iodide and 0.73 g (30 mg-atoms) of magnesium files in 20 ml of anhydrous ether, was added dropwise to 5 g (27 mmol) of ketone **20**-d_3 in 100 ml of anhydrous ether with vigorous stirring. After the addition the mixture was refluxed for 1 hr. The usual work-up and distillation of the crude product furnished 4.95 g of a 1:1 mixture of starting material (**20**-d_3) and hydroxy ester **21** which was separated by vpc on SE-30. **20**-d_3 (1.835 g) and **21** (1.970 g, 39.5% yield) were obtained. The latter had bp 64–65° (0.1 mm); n^{25}D 1.4565; ir ($CHCl_3$) 1040, 1125, 1725, 2230, 3250 cm^{-1}.

Ethyl (±)-Laurolenoate-1′′-d_3 (22-d_3). Hydroxy ester **21** (1.5 g) was stirred together with a few crystals of iodine for 1 hr at 90–100°. The cooled mixture was taken up in ether and washed with 10% sodium bisulfite solution and with water. The ethereal layer was then dried over magnesium sulfate and concentrated. Distillation of the residue gave in quantitative yield (vpc of the crude product on 20 M/W and SE-30 at 160°) the ester **22**-d_3: bp 43–44° (0.1 mm); n^{21}D 1.4522; ir ($CHCl_3$) 1070, 1175, 1730, 2860, 2920, 2960 cm^{-1}; nmr ($CDCl_3$) δ 1.23 (t, J = 7 cps, 3 H), 1.55 and 1.65 (two broad "s," 3 H each), 4.11 (q, J = 7 cps, 2 H); mass spectrum, 100% d_3.[5,49]

(±)-Laurolenol-1′′-d_3 (18-d_3). The procedure as described for the lithium aluminum hydride reduction of **16**, but using the ester **22**-d_3, was employed: ir ($CHCl_3$) 1050, 2060, 2210, 3360 cm^{-1}; mass spectrum, 100% d_3.[5,49]

(±)-Laurolenal-1′′-d_3 (8-d_3). The procedure as described for the oxidation of **18**, but using alcohol **18**-d_3, was employed: ir ($CHCl_3$) 1660, 1720, 2050, 2120, 2690, 2790 cm^{-1}; mass spectrum, 100% d_3.[5,49]

Irradiation of Aldehydes 8, 8-d_1, and 8-d_3. (a) A solution of 1.0 g (7.2 mmol) of (+)-laurolenal **8** in 50 ml of pentane was placed in a cylindrical reactor equipped with a central 80-W lamp in a water-cooled Pyrex finger, and flushed thoroughly with argon. The solution was stirred magnetically at room temperature and irradiated for 6 hr. Vpc on UCON at 150° showed that the aldehyde had decarbonylated completely to **1,2,3-trimethylcyclopent-1-ene** (**29**). The solvent was removed by distillation through a Vigreux column. Distillation of the residue gave 570 mg (72% yield) of *S*-(−)-**29** of bp 118–119° (760 mm); d^{24} 0.795; n^{23}D 1.4384; $[\alpha]^{23}$D −46.0° (neat); ir ($CHCl_3$) 1450, 1570, 1580 cm^{-1}; nmr ($CDCl_3$) δ 0.97 (d, J = 6.5 cps, 3 H), 1.57 (broad "s" with fine splitting, 6 H); mass spectrum, see A (Figure 3).

Anal. Calcd for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 87.01; H, 12.83.

(b) Portions (20 ml) of a 2% solution of (+)-laurolenal (**8**) in hexane were flushed thoroughly with argon and irradiated in Pyrex tubes in the merry-go-round reactor (Pyrex filter). After different periods of irradiation the tubes were removed, and the solvent was distilled off. The remaining starting aldehyde was recovered from the photolysis mixture by vpc on 20 M/W at 150° in each case, and the specific rotations were measured; see Table III.

Table III. Specific Rotation of Recovered (+)-Laurolenal (**8**) after Different Irradiation Periods

Photolysis period, min	Photolytic conversion of **8**, %	$[\alpha]^{23}$D of recovered **8**, deg
12	12	+596.4
24	23	+601.2
36	36	+599.5
48	45	+597.5
60	55	+600.0

(c) Solutions (2%) of (+)-laurolenal (**8**) in isopropyl alcohol ethanol, and benzene were irradiated as in (a). In each case decarbonylation to **29** occurred exclusively (vpc analysis) and at comparable rates.

(d) Degassed samples of 0.1 *M* (+)-laurolenal (**8**) in hexane containing from 0.02 to 5.0 *M* *cis*-1,3-pentadiene and 0.5 and 1 *M* naphthalene, respectively, and one sample in neat *cis*-1,3-pentadiene solution were irradiated in Pyrex tubes in the merry-go-round reactor using an acetone filter solution. Vpc analysis (UCON at 150°) after 15% conversion of aldehyde revealed no difference in reaction rates relative to a parallel run in pure hexane. In addition, vpc screening (on TCEP at 35°) of the irradiated samples for *trans*-1,3-pentadiene showed that the *cis*-diene had not been isomerized.

(e) Attempts to sensitize the photodecarbonylation included acetophenone, benzene, and acetone as sensitizers. A 2% solution of (+)-laurolenal (**8**) in a 1:1 mixture of pentane–acetophenone (4.2 *M*) was irradiated for 12 hr as in (a). No trace of reaction could be detected by vpc.

Two samples of 50 mg (0.36 mmol) of (+)-laurolenal (**8**) in 2 ml of benzene and 2 ml of pentane, respectively, were placed in quartz tubes, carefully flushed with argon, then closed and stirred magnetically at room temperature. Each tube was irradiated for 40 hr with an external low-pressure lamp, main emission at 2537 Å (equal geometry in both runs; in the case of the pentane sample the lamp was additionally surrounded by a 1-cm benzene filter). In the benzene run 12% of aldehyde **8** had been consumed, and about 8% decarbonylation product **29** had formed. In the pentane run considerably less aldehyde had been consumed, so that only traces of **29** were detectable by vpc (UCON at 130°).

A solution of 100 mg (0.72 mmol) of (+)-laurolenal (**8**) in 5 ml of acetone was degassed in a quartz tube and irradiated with 2537 Å as above for 8 hr. The irradiated sample was colored yellowish. Vpc on UCON at 150° showed that the aldehyde had reacted completely and a trace of **29** had been formed. The crude reaction mixture could not be distilled at 0.01 mm.

(f) Photolyses of (+)-aldehyde **8**-d_1 (100% d_1[5]) were carried out in pentane and in isopropyl alcohol as described in (a). In each case decarbonylation to **1,2,3-trimethylcyclopent-1-ene-3-d_1** (**29**-d_1), 100% d_1,[5,49] was observed exclusively: nmr ($CDCl_3$) δ 0.97 (s, 3 H), 1.57 (broad "s" with fine splitting, 6 H).

(g) A solution of 60 mg (0.434 mmol) of **8** and 60 mg (0.431 mmol) of **8**-d_1 in 2 ml of pentane in a Pyrex tube was carefully flushed with nitrogen, then closed with a rubber cap and irradiated with an external 80-W lamp, with magnetic stirring at room temperature. At intervals 200-μl portions of the solution were removed with a syringe, and starting aldehydes (**8** and **8**-d_1) and decarbonylation products (**29** and **29**-d_1) were isolated by vpc (SE-30 at 110°) and analyzed by mass spectrometry; see Table IV.

Table IV. Composition of the Aldehyde (**8** + **8**-d_1) and Decarbonylation Product (**29** + **29**-d_1) Fractions in the Photolysis of the Mixture **8** + **8**-d_1[a]

Photolysis period, min	Ratio **8**-d_1:**8**	Ratio **29**-d_1:**29**
0	1.0:1.0	
60	1.0:1.0	
120	1.06:1.0	
150	1.06:1.0	1.0:1.14
180	1.05:1.0	1.0:1.14

[a] Data of irradiation experiment g.

(h) A 1-ml solution of 0.72 *M* (+)-laurolenal (**8**) and 0.34 *M* tri-*n*-butylstannane in pentane was degassed and sealed in a Pyrex tube, and then irradiated with an external 125-W lamp with magnetic stirring at room temperature. Periodical vpc analyses (UCON at 180°) showed that decarbonylation to **29** was paralleled by reduction to alcohol **18** in a constant ratio of 1:1.3 throughout the entire photolysis. Dark reduction of **8** to **18** by stannane in parallel test runs was 10–15% of the reduction in the photolytic runs. Each value for photoreduction given here and in experiments i and j is corrected for concurrent dark reduction. Alcohol **18** was isolated by vpc from the photomixture and identified by ir and nmr spectra.

(i) (+)-Aldehyde **8**-d_1 was irradiated in pentane containing tri-*n*-butylstannane as described for **8** in (h). The reaction was completed after 7.5 hr. The resulting **laurolenol-1′-d_1** (**18**-d_1) was isolated directly by vpc (UCON at 180°) from an aliquot of the crude photolyzed solution which contained a 1:1.3 ratio of products **29**-d_1 and **18**-d_1. Mass spectral analysis of **18**-d_1 showed a deuterium content of 100% d_1.[5,49] Another aliquot was subjected to molecular distillation to separate 1,2,3-trimethylcyclopent-1-ene-3-d_1 (**29**-d_1). Subsequent purification by vpc (UCON at 100°) and mass spectral analysis indicated a deuterium content of 91.2% d_1[5,49] for **29**-d_1.

From a parallel run with 0.57 *M* **8**-d_1 and 2.17 *M* stannane in pentane which had been interrrupted after a 50% conversion of **8**-d_1, the remaining aldehyde was recovered by vpc (UCON at 180°) and analyzed by mass spectrometry; the deuterium content (100% d_1[5,49]) was unchanged.

In a third run with 0.57 *M* **8**-d_1 and 2.17 *M* stannane in pentane the products **18**-d_1 and **29**-d_1 were formed in the ratio 2.1:1, and the isotopic purity of **29**-d_1 was 90.5% d_1.[5,49]

(j) Two degassed 1-ml solutions of 0.72 *M* (+)-aldehyde **8**-d_1 and 0.34 *M* tri-*n*-butylstannane each, and of 0.5 and 1 *M* naphthalene, respectively, in pentane in Pyrex tubes were irradiated together with a parallel run without naphthalene in the merry-go-round reactor using an acetone filter solution. The conversion of aldehyde was completed simultaneously in all three samples, and vpc analysis (UCON at 180°) showed identical product compositions: 1.3:1 ratio of **18**-d_1 and **29**-d_1.[49] The products were isolated as described in (i) and had mass spectrometrically determined deuterium contents of 100% (**18**-d_1) and 91% d_1 (**29**-d_1).[5]

(k) Two degassed 0.724 *M* solutions of (+)-laurolenal (**8**) in pentane were irradiated separately with monochromatic light of 2804 (half-width 5.0 mμ) and 3341 Å (half-width 0.5 mμ; both wavelengths isolated from an HBO 500-W Osram mercury high-pressure lamp through a Bausch and Lomb monochromator). With 2804 Å a 50% conversion of aldehyde was reached after 120 hr, and with 3341 Å complete conversion after 51 hr. The solvent was removed at reduced pressure, and product **29** was isolated by distillation and subsequent vpc purification (NPGS, 100°). See Table V for the optical rotations of the two samples of **29**.

Table V. Photodecarbonylation (+)-**8** → (−)-**29**. Dependence of Racemization on Wavelength of Excitation[a]

λ of optical rotatory measurement, mμ	$\alpha^{23.5°}$ of **29** obtained from irradiation at 2804 Å, deg	3341 Å, deg
365	−15.605	−14.700
405	−11.015	−10.375
436	−8.765	−8.260
546	−4.660	−4.390
589	−3.820	−3.600

[a] Data of irradiation experiment (k); α determined of pure liquid; relative error ±0.010°.

(l) Two degassed solutions of 0.86 *M* (+)-**8**-d_1 and 1.0 *M* stannane were irradiated separately in quartz tubes with 2804 and 3341 Å, respectively, as described in (k). The irradiations were stopped at *ca.* 20% product **29**-d_1 formation in each case. Isolation of **29**-d_1 involved molecular distillation and subsequent vpc purification (NPGS, 100°). Mass spectrometry indicated the following isotope compositions: **8**-d_1 98.7% d_1 (before and after irradiation), **29**-d_1 77.4% d_1 from the run with 2804 Å, and 90.0% d_1 with 3341 Å.[5,49]

(m) A solution of 1.0 g (7.2 mmol) of aldehyde (±)-**8**-d_3 in 50 ml of pentane was irradiated as described in (a). The resulting mixture of **1,2,3-trimethylcyclopentene-1′**-d_3 (**31**) and -3′-d_3 (**30**)[49] had mass spectrum B (Figure 3):[23] nmr (CDCl$_3$) δ 0.97 (d, *J* = 6.5 cps, *sec*-methyl signal strongly reduced in intensity relative to the spectrum of **29**), 1.57 (broad "s" with fine splitting, intensity slightly reduced). A quantitative estimate of the composition of the photomixture **30** + **31** was made by nmr analysis of its ozonization product. Prior to this experiment, 2 g (18 mmol) of nondeuterated compound **29** (obtained from the photolysis of (+)-**8**) was ozonized at −70° in 30 ml of pentane. The blue-colored solution was brought to room temperature, and the solvent was distilled off over a Vigreux column. The remaining ozonide was dissolved in 30 ml of methanol and hydrogenated over 150 mg of palladium catalyst on calcium carbonate (10%). Hydrogen (335 ml) was absorbed (calcd. 405 ml). The catalyst was removed by filtration and the solvent evaporated at slightly reduced pressure. Distillation of the residue gave 2.098 g (78% yield) of **3-methylheptane-2,6-dione** (**35**), bp 75–76° (4 mm). The analytical sample was purified by vpc on UCON at 150°: ir (CHCl$_3$) 1715 cm^{-1}; nmr (CDCl$_3$) δ 1.10 (d, *J* = 7 cps, 3 H), 2.14 + 2.16 (2 s, 3 H each) (see Figure 2A); mass spectrum, *m/e* 142 (M$^+$, $C_8H_{14}O_2$), 43 (base peak).

The same procedure applied to the ozonization and work-up of the mixture **30** + **31** yielded a mixture of **trideuterated 3-methylheptane-2,6-diones 36** and **37** (bp 75–76° at 4 mm; ir (CHCl$_3$) 1710, 2070, 2120, 2220 cm^{-1}). Mass spectrometry showed a content of 91.2% d_3, 5.1% d_2, 2.3% d_1, and 1.4% d_0.[5,49] The quantitative determination on the basis of nmr integration (see Figure 2B) gave 88.7 ± 0.5% **36** and 11.3 ± 0.5% **37**.

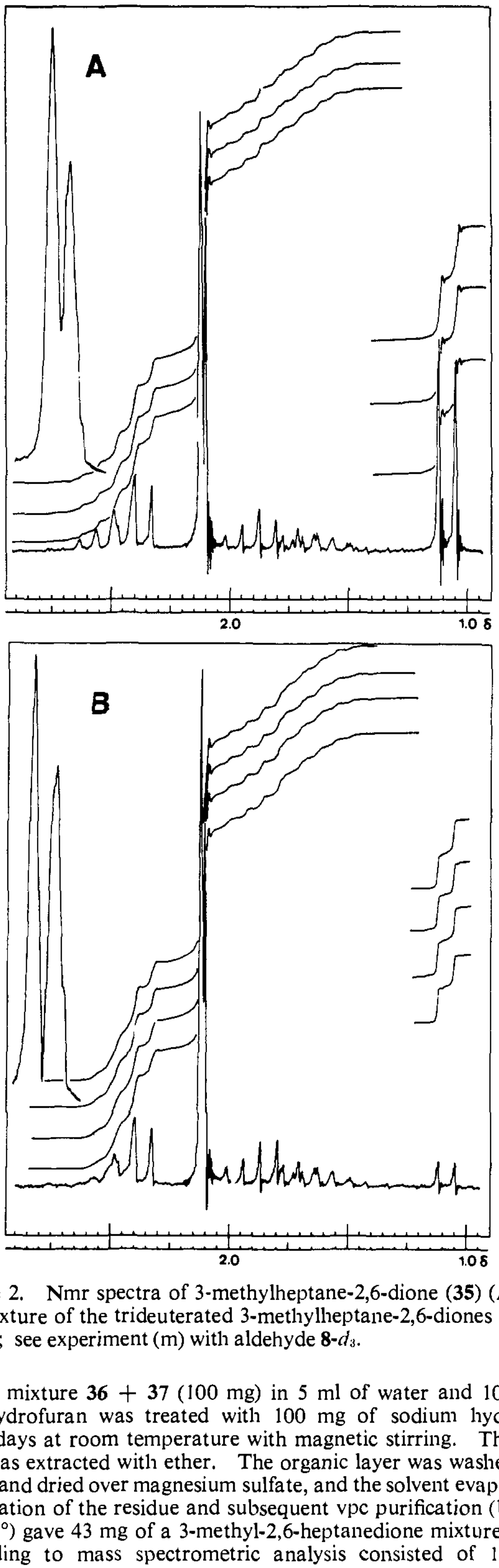

Figure 2. Nmr spectra of 3-methylheptane-2,6-dione (**35**) (A) and the mixture of the trideuterated 3-methylheptane-2,6-diones **36** and **37** (B); see experiment (m) with aldehyde **8**-d_3.

The mixture **36** + **37** (100 mg) in 5 ml of water and 10 ml of tetrahydrofuran was treated with 100 mg of sodium hydroxide for 2 days at room temperature with magnetic stirring. The mixture was extracted with ether. The organic layer was washed with water and dried over magnesium sulfate, and the solvent evaporated. Distillation of the residue and subsequent vpc purification (UCON at 150°) gave 43 mg of a 3-methyl-2,6-heptanedione mixture which according to mass spectrometric analysis consisted of 12% d_0 (**35**) and 88% d_3[5] components (**36**).

(n) A 2-ml solution of 0.288 *M* (+)-**8**-d_1 and 0.284 *M* (±)-**8**-d_3 in pentane was irradiated as described in (j) until the aldehyde conversion had reached 75%. The product was isolated by vpc (UCON at 100°). Mass spectrometry showed the exclusive presence of d_1 (**29**-d_1) and d_3 components (**30** and **31**).[49]

Attempted Sensitization of (+)-1,2,3-Trimethylcyclopentene (29). Solutions of 2.5 g of (+)-compound **29** ($[\alpha]^{23}{}_{546}$ +7.93°, $[\alpha]^{23}{}_{D}$ +6.53°, both measurements with liquid sample;[53] material prepared by pyrolysis of camphanic acid according to Aschan[56]) in 5

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(56) O. Aschan, *Ann.*, **290**, 187 (1895).

ml of benzene and 5 ml of toluene, respectively, were irradiated for 100 hr each at room temperature in quartz tubes with an external low-pressure lamp (equal geometry in both runs). Photolytic decompositions of the starting material were very slow in both cases. Recovery of **29** by vpc (UCON at 100°) and determination of the rotatory power revealed that in both samples the initial optical activity was preserved.

Degradation of (−)-Photoproduct 29 to (*R*)-(−)-3-Methylheptane (34). (+)-Laurolenal (5.345 g, 38.7 mmol) (**8**; optical activity 96.3 ± 1.4% of the absolute value, *vide supra*) was photolyzed in 150 ml of pentane under argon atmosphere as described in (a). After total conversion to **29** (vpc analysis) the solution was concentrated to *ca.* 50-ml volume and ozonized at −70° until the blue color persisted. A precooled solution of 2 g (52.6 mmol) of lithium aluminum hydride in 80 ml of anhydrous ether was then added. The mixture was stirred overnight and gradually warmed up to room temperature. The usual work-up furnished 3.150 g (56% yield) of (3*S*)-(+)-**3-methylheptane-2,6-diol** (**32**) after distillation of the crude product: bp 83–84° (0.1 mm); ir ($CHCl_3$) 1050, 3320 cm^{-1}; $[\alpha]^{23}\mathrm{D}$ +2.21° (*c* 1.5, EtOH); nmr ($CDCl_3$) δ 0.90 + 1.15 + 1.20 (three d, each *J* = 6 cps and 3 H), 3.75 (b, 2 H).

Diol **32** (3.050 g (20.8 mmol)) was esterified at 0° with 10 g (50 mmol) of *p*-toluenesulfonyl chloride in 50 ml of pyridine under stirring overnight. Ice water was added, and the mixture was extracted with ether after acidification with 2 *N* hydrochloric acid, 7.560 g (82% yield) of a brown oil ((3*S*)-(+)-**3-methylheptane-2,6-diol di-*p*-toluenesulfonate** (**33**), ir ($CHCl_3$) 890, 1242, 1351 cm^{-1}) was obtained.

The crude di-*p*-toluenesulfonate (**33**) (7.560 g, 17 mmol) was reduced in 100 ml of anhydrous ether with 1.5 g (40 mmol) of lithium aluminum hydride at room temperature. After stirring overnight, the usual work-up and purification by preparative vpc on UCON at 100° gave 485 mg (25% yield) of (*R*)-(−)-**3-methylheptane** (**34**), bp 116–117° (760 mm); $n^{23}\mathrm{D}$ 1.3965; d^{23} 0.7161; ir (film) 1380, 1460, 2860, 2920, 2950 cm^{-1}; nmr ($CDCl_3$) two broad signals at δ 0.90 and 1.25; $\alpha^{24}{}_{365}$ −0.805°, $\alpha^{24}{}_{405}$ −0.750°, $\alpha^{24}{}_{436}$ −0.695°, $\alpha^{24}{}_{546}$ −0.570°, $\alpha^{24}\mathrm{D}$ −0.525° (all measurements with liquid sample[53]); $\alpha^{24}\mathrm{D}$ −0.526° (extrapolated value); $[\alpha]^{24}\mathrm{D}$ −7.35 ± 0.05° (calcd from the extrapolated value of $\alpha\mathrm{D}$ and *d*).

Anal. Calcd for C_8H_{18}: C, 84.12; H, 15.88. Found: C, 84.14; H, 15.78.

The degradation product **34** was identified by direct comparison with a commercially available sample of racemic 3-methylheptane (ir, film) and with a sample of (*S*)-(+)-3-methylheptane ($[\alpha_{\mathrm{abs}}]^{25}\mathrm{D}$ +10.12 ± 0.1°, liquid) provided by Professor Pino[21,22] (comparison by vpc (SE-52 column, 60°) and mass spectra, *m/e* 114 (M^+)). The $[\alpha]\mathrm{D}$ values of the two samples establish an enantiomeric purity of 72.6 ± 1.5% of the degradation product, hence a racemization of 27.4 % during the photolysis of **8**.

Mixture of Ethyl *cis*- and *trans*-(±)-2,5-Dimethylcyclopentan-1-one-2-carboxylates (20).[57a] Keto ester **19** (12.1 g, 71 mmol) was methylated with methyl iodide using the procedure described for the preparation of **20**-d_3. Distillation of the crude product afforded 11.96 g (92% yield) of a fraction of bp 52–53° (0.15 mm); $n^{21}\mathrm{D}$ 1.4330; ir ($CHCl_3$) 992, 1175, 1262, 1735, 1755 cm^{-1}; the nmr ($CDCl_3$, 100 Mcps) showed the presence of a *ca.* 1:1 mixture of diastereoisomers: δ 1.12 and 1.19 (two d, *J* = 7 cps, 3 H), 1.24 (t, *J* = 7 cps, 3 H), 1.27 and 1.33 (two s, 3 H), 4.12 and 4.14 (two q, *J* = 7 cps each, 2 H); mass spectrum, *m/e* 184 (M^+, $C_{10}H_{16}O_3$). Vpc on UCON at 180° did not resolve the two components.

Diastereoisomeric Ethyl (±)-1,3-Dimethyl-2-methylenecyclopentane-1-carboxylates (23). The entire reaction was performed in a carefully dried system which was kept constantly under pure nitrogen atmosphere. Ammonia (250 ml), which had been pretreated with sodium until the blue color persisted, was condensed and a small amount of sodium and 10 mg of pulverized ferric nitrate were added. The solution turned dark blue and in a few minutes to light grey. Sodium (1.3 g, 56 mg-atoms) was added in small portions to form a dark-grey solution of sodium amide within 15 min. On treatment with 12 g (33 mmol) of triphenylmethylphosphonium bromide, the yellow ylide formed instantaneously, and the excess ammonia was evaporated by warming the mixture lightly. The solid residue was taken up in 200 ml of anhydrous ether and refluxed for 15 min before the suspension was filtered through a glass filter. The filtrate was treated dropwise with 4.60 g (25 mmol) of the keto ester mixture **20** in 20 ml of anhydrous ether at room temperature and then refluxed overnight. The ether was distilled off and the residue was subjected to a molecular distillation at 10^{-5} mm pressure to remove the product from triphenylphosphine oxide. The distillate was fractionated once more to give 3.055 g (67 % yield) of a binary mixture **23**, bp 80–82° (9 mm). Vpc analysis (20 M/W at 150°) showed the presence of two components in a 19:1 ratio (relative retention times 1 and 1.4, respectively), which were separated by preparative vpc: major compound, ir ($CHCl_3$) 894, 1145, 1178, 1263, 1650, 1731, 2868, 2960, 3078 cm^{-1}; nmr ($CDCl_3$) δ 1.10 (d, *J* = 8 cps, 3 H), 1.21 (t, *J* = 7 cps, 3 H), 1.32 (s, 3 H), 4.06 (q, *J* = 7 cps, 2 H), 4.85 + 4.96 (two d, *J* = 3 cps, 1 H each); mass spectrum, *m/e* 182 (M^+, $C_{11}H_{18}O_2$); minor compound, nmr ($CDCl_3$) δ 1.09 (d, *J* = 8 cps, 3 H), 1.23 (t, *J* = 7 cps, 3 H), 1.28 (s, 3 H), 4.08 (q, *J* = 7 cps, 2 H), 4.85 + 4.96 (two d, *J* = 3 cps each, 1 H each); mass spectrum, pattern identical with that of major product.

(±)-1-Hydroxymethyl-1,3-dimethyl-2-methylenecyclopentane (24). The reduction of the ester **23** with lithium aluminum hydride was carried out as described for **16 → 18**. Alcohol **24** was obtained in 93% yield: bp 48° (1.5 mm); ir ($CHCl_3$) 888, 1032, 1650, 3070, 3360 (broad) cm^{-1}; nmr ($CDCl_3$) 1.03 (s, 3 H), 1.10 (d, *J* = 8 cps, 3 H), 3.31 and 3.40 (two d, each *J* = 11 cps and 1 H), 4.78 and 4.88 (two d, each *J* = 3 cps and 1 H); mass spectrum, *m/e* 140 (M^+, $C_9H_{16}O$).

(±)-1-Hydroxymethyl-1,3-dimethyl-2-methylenecyclopentane-1′,1′-d_2 (24-d_2). The procedure as described for **16 → 18**, but using ester **23** and lithium aluminum deuteride, was employed. Compound **24**-d_2 had bp 82–83° (10 mm); $n^{24}\mathrm{D}$ 1.4670; ir ($CHCl_3$) 885, 1645, 2080, 2190, 3060, 3350 (broad) cm^{-1}; nmr ($CDCl_3$) δ 1.05 (s, 3 H), 1.10 (d, *J* = 6.5 cps, 3 H), 4.85 and 4.94 (two d, each *J* = 2.5 cps and 1 H); mass spectrum, 100 % d_2.[5,49]

(±)-1-Formyl-1,3-dimethyl-2-methylenecyclopentane (9). The oxidation of alcohol **24** was carried out as described for **18 → 8**, furnishing aldehyde **9** in 89% yield: bp 63–64° (10 mm); uv, see Table I; ir ($CHCl_3$) 896, 1645, 1729, 2700, 3078 cm^{-1}; nmr ($CDCl_3$) δ 1.13 (d, *J* = 7 cps, 3 H), 1.22 (s, 3 H), 4.85 and 5.05 (two d, each *J* = 2.4 cps and 1 H), 9.30 (s, 1 H); mass spectrum, *m/e* 138 (M^+, $C_9H_{14}O$), 109 (M^+ − CHO, base peak).

(±)-1-Formyl-1,3-dimethyl-2-methylenecyclopentane-1′-d_1 (9-d_1). The oxidation of the alcohol **24**-d_2 was carried out as described for **18 → 8**. Aldehyde **9**-d_1 had bp 69–70° (10 mm); $n^{24}\mathrm{D}$ 1.4555; uv (EtOH) max 295 (ε 70), (isooctane) 300 mμ (ε 63); ir ($CHCl_3$) 895, 1645, 1710, 2045, 2100, 3060 cm^{-1}; nmr ($CDCl_3$) δ 1.12 (d, *J* = 7 cps, 3 H), 1.22 (s, 3 H), 4.85 and 5.05 (two d, each *J* = 2.4 cps and 1 H); mass spectrum, *m/e* 139 (M^+, $C_9H_{13}DO$), 100% d_1.[5,49]

Irradiation of Aldehydes 9 and 9-d_1. (a) A solution of 153 mg (1.11 mmol) of aldehyde **9** in 15 ml of pentane was irradiated at room temperature in a quartz tube and with an 80-W lamp.[57b] Both the tube and the lamp were placed at one of the focus points of an elliptical compartment of polished aluminum each. The solution was stirred with a stream of pure nitrogen. The aldehyde conversion was completed after 3 hr. Vpc analysis on UCON at 150° showed that at least 98% of the material formed was **1,2,3-trimethylcyclopent-1-ene** (**29**, 28%) and **1,3-dimethyl-2-methylenecyclopentane** (**38**, 72%); nmr (CCl_4) δ 1.05 (d, *J* = 6.5 cps, 6 H), *ca.* 1.25 (m, 2 H), 4.73 (t, *J* = 2.5 cps, 2 H); mass spectrum, *m/e* 110 (M^+, C_8H_{14}), 95 (base peak).

(b) Degassed 5-ml samples of 600 mg (4.32 mmol) of aldehyde **9**-d_1 in pentane and in pentane containing 1.5 g (5.15 mmol) of tri-*n*-butylstannane, respectively, were irradiated in the merry-go-round reactor (Pyrex filter) for 10 hr. The products were **1,3-dimethyl-2-methylenecyclopentane-1-d_1** (**38**-d_1; mass spectrum, deuterium content 100 % d_1[5,49] in both runs) and **1,2,3-trimethylcyclopent-1-ene-2′-d_1** (**39**; mass spectrum, deuterium content 90% d_1 in the sample run in pure pentane, and 78% d_1 in the sample run in the presence of stannane;[5,49] see Figure 3, C and D). The product ratio **38**-d_1:**39** was 2.25:1 and 2.05:1, respectively. For the purpose of product isolation, the pentane solution was concentrated, and the residue distilled and subsequently separated by vpc (UCON, 80°). The stannane run was subjected to a molecular distillation prior to vpc separation.

Methyl 7-Methylenebicyclo[2.2.1]heptane-1-carboxylate (26).[57c] To a solution of 198 g (0.95 mol) of a mixture of *cis*- and *trans*-hexahydroterephthalic acid dichloride[58] in 1.3 l. of anhydrous boiling ether, 100 ml (0.72 mol) of triethylamine in 240 ml of ether was added dropwise over 45 min. The reaction mixture was refluxed

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(57) Preliminary experiments in the Diploma Theses, ETH, Zürich, by (a) P. Früh, 1967; (b) P. Gull, 1968; (c) B. Martinoni, 1968.

(58) R. Malachowski, S. J. Wasowska, and S. Jozkiewicz, *Ber.*, **71B**, 759 (1938). The preparation of keto ester **25** from hexahydroterephthalic acid dichloride was carried out by R. Pfeiffer, Diploma Thesis, ETH, Zürich, 1968.

for 20 hr with stirring. The ether was then removed under reduced pressure and a mixture of 90 ml of pyridine and 330 ml of methanol was added slowly at room temperature. After stirring for 14 hr, the solution was diluted with ether, washed consecutively with dilute sulfuric acid and with water, dried over magnesium sulfate, and taken to dryness *in vacuo*. Distillation of the residue at 0.7 mm and 73° furnished 41.3 g of a 2:1 mixture of hexahydroterephthalic acid dimethyl ester and **methyl bicyclo[2.2.1]heptan-7-one-1-carboxylate (25)** which was separated by a subsequent distillation in a spinning band column. Pure keto ester **25** (6 g) was obtained: mp 34°; bp 63° (0.1 mm); uv (EtOH) max 287 mμ (ϵ 20); ir (film) 1028, 1108, 1223, 1730, 1781 cm^{-1}; nmr (CDCl$_3$) δ 3.77 (s, 3 H).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19; O, 28.54. Found: C, 64.00; H, 7.26; O, 28.78.

For the conversion **25** → **26** the Wittig procedure described for the preparation of **23** was employed. Keto ester **25** (4.55 g, 27 mmol) in 20 ml of anhydrous ether was allowed to react with ylide prepared from 12 g (33 mmol) of triphenylmethylphosphonium bromide. Distillation of the crude product gave 3.96 g (89%) of **26**: bp 43° (0.05 mm); ir (film) 890, 1055, 1100, 1227, 2840, 2865, 3070 cm^{-1}; nmr (CDCl$_3$) δ 1.2–2.2 (m, 8 H), 2.53 (t, J = 3 cps, with fine splitting, 1 H), 3.76 (s, 3 H), 4.69 + 4.74 (two s, 1 H each); mass spectrum, *m/e* 166 (M$^+$, $C_{10}H_{14}O_2$).

1-Hydroxymethyl-7-methylenebicyclo[2.2.1]heptane (27).[57c] Ester **26** (2.715 g (16 mmol)) was reduced with 2 g (51 mmol) of lithium aluminum hydride in 60 ml of anhydrous ether at reflux temperature for 1 hr. To the cooled solution an excess of 2 *N* aqueous Seignette salt solution was added slowly under stirring. The organic layer was washed with aqueous saturated sodium chloride solution, dried over magnesium sulfate, and concentrated at reduced pressure. Distillation of the residue at 0.1 mm gave 2.105 g (94% yield) of a viscous oil (**27**): bp 57°; ir (CHCl$_3$) 890, 1015, 1680, 2860, 3060, 3610 cm^{-1}; nmr (CDCl$_3$) δ 1.3–1.8 (m, 8 H), 2.39 (t, J = 3 cps, with fine splitting, 1 H), 3.84 (s, 2 H), 4.52 + 4.62 (two s, 1 H each); mass spectrum, *m/e* 138 (M$^+$, $C_9H_{14}O$), 79 (base peak).

1-Formyl-7-methylenebicyclo[2.2.1]heptane (10).[57c] The procedure described for the preparation of **8** was employed. Alcohol **27** (2.041 g (15 mmol)) yielded after distillation of the crude product 1.895 g (95% yield) of aldehyde **10** which was further purified by preparative vpc on UCON at 160°: bp 38° (2 mm); uv, see Table I; ir (film) 890, 1680, 1720, 2700, 2860, 3065 cm^{-1}; nmr (CDCl$_3$) δ 1.4–2.2 (m, 8 H), 2.55 (t, J = 3 cps, with fine splitting, 1 H), 4.67 + 4.83 (two s, 1 H each), 10.00 (s, 1 H); mass spectrum, *m/e* 136 (M$^+$, $C_9H_{12}O$), 108 (base peak).

Irradiation of Aldehyde 10.[57c] (a) A solution of 1.798 g (13.2 mmol) of aldehyde **10** in 100 ml of pentane was placed in a cylindrical reactor equipped with a central 125-W lamp in a water-cooled Pyrex finger and irradiated for 12 hr at room temperature. The solution was stirred by a stream of pure nitrogen through an inlet at the bottom. A precipitate formed which was not investigated further. The irradiated solution contained according to vpc (UCON at 160°) *ca.* 5% of unreacted aldehyde **10,** 30% of low boiling components which were not further investigated, and 65% of a further multicomponent mixture. The first two fractions were removed by molecular distillation, and from the residual third fraction the following three components were isolated by vpc (TCEP at 160°): **alcohol 27** (*ca.* 80%), **1-acetyl-7-methylenebicyclo[2.2.1]heptane (40)** (*ca.* 8%), ir (CHCl$_3$) 910, 1360, 1679, 1699, 3070 cm^{-1}; nmr (CDCl$_3$) δ 2.22 (s, 3 H), 2.50 (t, J = 4 cps, 1 H), 4.55 + 4.71 (two s, 1 H each); mass spectrum, *m/e* 150 (M$^+$, $C_{10}H_{14}O$, 4%), 135 (10%), 122 (34%), 107 (16%), 91 (12%), 79 (23%), 43 (base peak, 100%); **1-propionyl-7-methylenebicyclo[2.2.1]heptane (41)** (*ca.* 5%), ir (CHCl$_3$) 910, 1678, 1699, 3065 cm^{-1}; nmr (CDCl$_3$) δ 1.10 (t, J = 8 cps, 3 H), 2.56 (q, J = 8 cps, 2 H), 4.52 + 4.70 (two s, 1 H each); mass spectrum, *m/e* 164 (M$^+$, $C_{11}H_{16}O$, 8%), 136 (44%), 135 (base peak, 100%), 107 (80%), 91 (35%), 79 (70%), 57 (23%), 29 (36%).

(b) Degassed samples of 0.101 *M* aldehyde solutions (2 ml each) in isopropyl alcohol and in isopropyl alcohol containing varying amounts of 1,3-pentadiene, respectively, were irradiated in the merry-go-round reactor (Pyrex filter) for 11 hr. Vpc analysis on UCON at 180° showed that in isopropyl alcohol reduction to alcohol **27** was the predominant photoprocess. The conversion of aldehyde (%) decreased with increasing concentration of 1,3-pentadiene (*M*) as follows: 72% (0 *M*), 71% (0.001 *M*), 68% (0.01 *M*), 64% (0.02 *M*), 40% (0.04 *M*), 24 % (0.08 *M*), 20% (0.1 *M*).

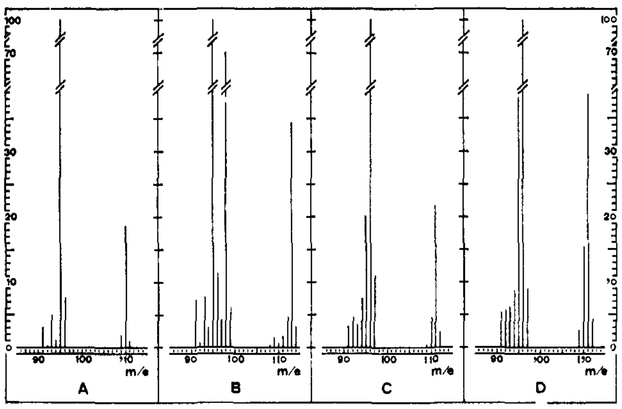

Figure 3. Mass spectra of: A, (−)-1,2,3-trimethylcyclopent-1-ene (**29**) from the photolysis of (+)-**8** (experiment a); B, mixture of 1,2,3-trimethylcyclopent-1-ene-3′-d_3 (**30**, 88.7%) and -1′-d_3 (**31**, 11.3%) from the photolysis of (±)-**8**-d_3 (experiment m); C, 1,2,3-trimethylcyclopent-1-ene-2′-d_1 (**39**) from the photolysis of (±)-**9**-d_1 in pentane (experiment b); D, 1,2,3-trimethylcyclopent-1-ene-2′-d_1 (**39**) from the photolysis of (±)-**9**-d_1 in pentane + tri-*n*-butylstannane (experiment b).

Quantum Yield Determination of the Photodecarbonylation of Aldehydes (±)-7 and *R*-(+)-8. The irradiation unit consisted of an optical bench with an Osram HBO 500-W high-pressure mercury lamp. Its full light emission was focussed by an appropriate system of mirror, quartz lenses, and a water-cooled quartz cell on the entrance slit of a Bausch and Lomb 500-mm grating monochromator. The monochromatic exit beam passed through two quartz cells (path length 1 cm each). The sample solutions had optical densities of *ca.* 2 at the wavelengths of the incident light. Prior to irradiation the solutions were degassed and transferred in an argon-filled glove box into the first 1-cm cell which was then sealed hermetically.

Optical densities were measured on a Zeiss spectrophotometer PMQ II.

The ferrioxalate method described by Parker and Hatchard[59] was employed for actinometry (0.15 *M* FeK[(COO)$_2$]$_2$ solution; $\phi_{Fe^{2+}}$ 1.24 at aboth 2970 and 3130 Å; photometric determination of the Fe^{2+}–1,10-phenanthroline complex at 5100 Å, ϵ 11,100 l. mol^{-1} cm^{-1}).

The quantum yields were measured at 20–40% conversion of the aldehydes 7 and **8**, as determined by the decrease of optical density at 3130 Å of the irradiated solutions. The incident light intensity was monitored before and after each irradiation experiment. The results are given in Table II.

Emission Measurements with (*R*)-(+)-Laurolenal (8). The measurements were conducted in an Aminco-Bowman fluorophosphorimeter. For phosphorescence a modified sample holder was used which is designed to ensure a reproducible position of the sample tube in the phosphoroscope.

(a) Solutions (10^{-2} *M*) of **8** exhibited neither fluorescence (solution in isopentane at room temperature) nor phosphorescence (EPA glass at 78°K) on excitation in the wavelength region 2800–3400 Å. (b) Phosphorescence of naphthalene was not sensitized on excitation in the region 3300–3400 Å at 10^{-1} *M* naphthalene and 10^{-2} *M* **8** in EPA glass at 78°K. (c) Phosphorescence of 10^{-3} *M* acetophenone was not quenched by 10^{-1} *M* **8** (EPA glass at 78°K) on excitation at 2880 Å.

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(59) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235,** 518 (1956).