Molecular Structure and Photochemical Reactivity. XI. Wavelength and Methyl Substituent Effects in the Photochemistry of Lactones in the Liquid Phase[1]

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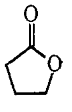
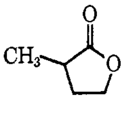
Abstract: The photochemistry of γ-butyrolactone (I) (2537 Å, liquid phase) is extended to α-methylbutyrolactone (II) and γ-methylbutyrolactone (III) to determine (1) the effect of replacing a hydrogen atom of γ-butyrolactone with a methyl group in the α (lactone II) and γ (lactone III) positions on product quantum yields and excited-state lifetimes, and (2) the effect on product quantum yields with a change in wavelength from 2537 to 2380 Å. A methyl group in the α position increases the Φ_{formate} from 0.23 (allyl formate) to 0.39 (crotyl formate), and the $\Phi_{\text{cyclopropane}}$ increases from 0.013 (cyclopropane) to 0.027 (methylcyclopropane) (2537 Å, 25°, neat) while the yield of the aldehyde products does not change (succinaldehyde and methylsuccinaldehyde). A methyl group in the γ position does not affect the Φ_{formate} significantly but $\Phi_{\text{pentanal-4-one}}$ is very much less than $\Phi_{\text{succinaldehyde}}$ and $\Phi_{\text{methylsuccinaldehyde}}$. A methyl group in the γ position decreases the lifetime of the excited state from 1.2×10^{-9} to 10^{-11} sec, but substitution in the γ position has only a small effect. The change in wavelength from 2537 to 2380 Å increases the yield of the dialdehydes ($\Phi^{2537}_{\text{succinaldehyde}} = 0.06$; $\Phi^{2380}_{\text{succinaldehyde}} = 0.11$; $\Phi^{2537}_{\text{methylsuccinaldehyde}} = 0.05$; $\Phi^{2380}_{\text{methylsuccinaldehyde}}$ 0.13), but does not change the quantum yield of formate or cyclopropane significantly. The possibility that this wavelength effect is due to vibrational effects in solution is discussed.

In the previous paper of this series, we presented a study of the photodecomposition of γ-butyrolactone (I) in the liquid phase.[2] This paper is an extension of that work and is concerned with (1) wavelength dependence of product quantum yields and (2) the effect of a methyl group in the α (lactone II) and γ (lactone III) positions on primary processes, quantum yields, and rates of excited lactone decomposition.


I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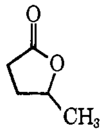
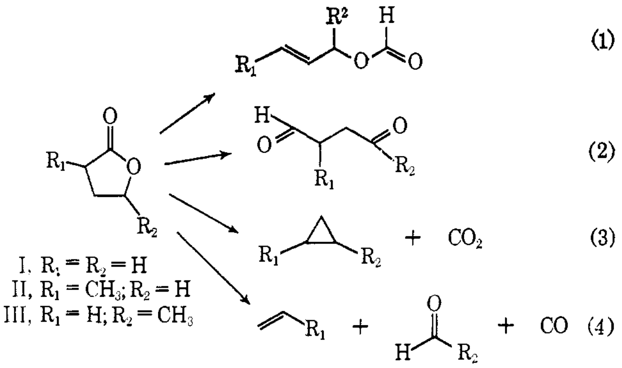

III

Results

Products and Primary Processes. The products obtained from I at 2537 Å have been previously reported.[2] The products from I at 2380 Å are the same, *i.e.*, allyl formate, succinaldehyde, cyclopropane, (carbon monoxide and carbon dioxide were not determined at 2380 Å), and small amounts of ethylene and propylene.

Irradiation of II with 2537 and 2380 Å radiation produced crotyl formate (*cis* + *trans*), methylsuccinaldehyde, methylcyclopropane, and small amounts of propylene and butene-2. The products identified from the irradiation of III at 2537 and 2380 Å are 3-but-2-enyl formate, methylcyclopropane, and small amounts of ethylene and possibly pentanal-4-one.

The observed major products can be accounted for by the primary processes 1–3.



The formation of small amounts of ethylene from I and III and propylene from II probably arises from process 4. Unfortunately the expected formaldehyde from I and II could not be detected. Some acetaldehyde formation was observed when III was irradiated, but the yield was very much smaller than the yield of ethylene. Preliminary results in the vapor-phase photodecomposition of I show that primary process 4 is important in the vapor phase, since equal amounts of ethylene, formaldehyde, and carbon monoxide were found. This suggests that olefins probably arise by process 4 in solution as well. The reason for the failure to observe the small amounts of aldehydes in solution phase cannot be given at this time.

The formation of small amounts of propylene from I and butene-2 may arise from a different primary process or from the same primary process which gives rise to cyclopropane.

Wavelength and Methyl Substituent Effects on Product Quantum Yields. Table I presents the quantum yields for products obtained from the photodecomposition of γ-butyrolactone (I), α-methylbutyrolactone (II), and valerolactone (III) at 2537 and 2380 Å.

The quantum yields of the products obtained from the methyl-substituted lactones (II and III) were not measured directly, but are based on the quantum yields of products obtained from γ-butyrolactone (I) at 2537 Å. Although the absolute values may have appreciable error, the relative quantum yields are quite reliable.

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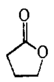
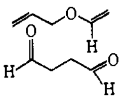
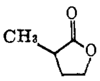
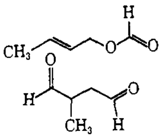
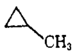
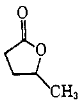
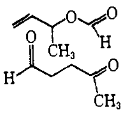
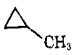
[1] This paper is taken from the Ph.D. dissertation of R. S., University of California, Riverside, Calif. 92502. He acknowledges with thanks an Air Pollution Special Predoctoral Fellowship.

[2] R. Simonaitis and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, 90, 1389 (1968).

Table I. Quantum Yields for Formation of Products at 25°[a,b]

Compd	Product	$\Phi_{2537\,\text{Å}}$	$\Phi_{2380\,\text{Å}}$
		0.23 0.06	0.21 0.11
		0.013	0.013
	C_2H_4	0.005	0.012
		0.39 0.05	0.36 0.13
		0.027	
		0.18 0.01[c]	0.21 0.016[c]
		0.004	
	C_2H_4	0.005	

[a] No attempt was made to analyze for CO or CO_2 from I at 2380 Å and from II and III at both wavelengths. [b] The quantum yields are for the neat lactones. [c] Identity of product not certain.

The quantum yields at 2380 Å (determined by relative measurements of light intensity and glpc areas) are also based on the absolute quantum yields at 2537 Å. The error present in the absolute quantum yields at 2537 Å is, of course, reproduced at 2380 Å, but the relative quantum yields are again much more accurate, since the ratio $\Phi_{\text{formate}}/\Phi_{\text{aldehyde}}$ was measured in the same run. Table II presents the ratio

$$\left(\frac{\Phi_{\text{formate}}}{\Phi_{\text{aldehyde}}}\right)_{2380\,\text{Å}} \Bigg/ \left(\frac{\Phi_{\text{formate}}}{\Phi_{\text{aldehyde}}}\right)_{2537\,\text{Å}}$$

and this data convincingly shows that there is a change in the product distribution with a change in wavelength.

Table II. Effect of Wavelength on Product Yields at 25°[a]

Run	$(\Phi_f/\Phi_a)_{2380\,\text{Å}}/(\Phi_f/\Phi_a)_{2537\,\text{Å}}$[b]	$(\Phi_f/\Phi_a)_{2380\,\text{Å}}/(\Phi_f/\Phi_a)_{2537\,\text{Å}}$[c]
1	0.42	0.38
2	0.50	
3	0.50	

[a] $\Phi_f = \Phi_{\text{formate}}$; $\Phi_a = \Phi_{\text{aldehyde}}$. [b] For lactone γ-butyrolactone (I). [c] For lactone α-methylbutyrolactone (II).

Since the molar absorptivity at 2380 Å is much greater than at 2537 Å, the local rates of product formation will be different at these two wavelengths because of the light intensity variation along the cell. The question then arises as to whether the observed "wavelength effect" is not in reality an "intensity" effect. We were unable to vary the intensity over a sufficient range to test this, but an intensity effect seems unlikely because (1) no free radicals are involved and (2) biphotonic processes are extremely unlikely.

A more likely possibility that needs to be considered is that the larger effective conversions in the front of the cell in the 2380-Å experiments may cause a reduction in the formate yield because of quenching, secondary photolysis, or other effects, thus causing a change in $\Phi_{\text{formate}}/\Phi_{\text{aldehyde}}$ with a change in wavelength (the yield of allyl formate decreases rapidly with extent of conversion at 2537 Å).[2] The fact that the absolute yield of the aldehyde increases and the formate yield is virtually unchanged with decreasing wavelengths shows that the change in $\Phi_{\text{formate}}/\Phi_{\text{aldehyde}}$ is not due to a decrease in the formate yield.

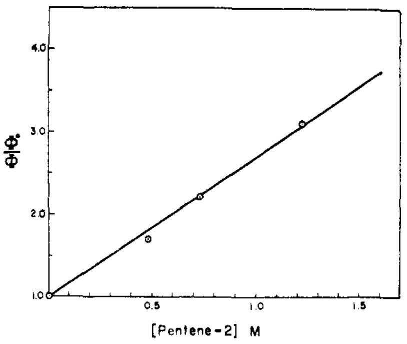


Figure 1. Stern–Volmer plot for quenching of 3-but-2-enyl formate with pentene-2.

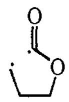
Substitution of a methyl group in the α position increases the quantum yield for formate and cyclopropane formation, but does not appreciably alter the aldehyde yield. However, substitution in the γ position reduces or completely eliminates the aldehyde yield (see Experimental Section) and reduces the yield of cyclopropane, but does not affect the yield of formate significantly.

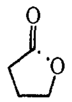
Quenching Experiments. In the earlier work we found that olefins quench the triplet state of γ-butyrolactone at diffusion-controlled rates[2] and here we present the effect of pentene-2 on product yields for α-methylbutyrolactone and valerolactone.

Addition of pentene-2 (1.3 *M*) to α-methylbutyrolactone had virtually no effect on product yields ($\Phi^0/\Phi_{\text{formate}} = 1.1 \pm 0.2$), but addition of pentene-2 to valerolactone reduced the yield of 2-but-3-enyl formate. Figure 1 presents a Stern–Volmer plot for the quenching of this formate. The Stern–Volmer quenching constant obtained from this plot is 1.7 *M*.[3]

Discussion

Substituent Effects on Product Quantum Yields. We have previously suggested that the formation of the products proceeds through diradical intermediates A and B. If this is true, then the fact that the quantum yields for product formation are less than unity (~0.5) is probably due to the back reaction of diradicals A and B to give starting material with the quantum yield for diradical formation being close to unity.[4] The increased yield of formate and cyclopropane formation upon methyl substitution in the α position is then due to either a decrease in the rate of the back-reaction or


A


B

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[3] The addition of pentene-2 to valerolactone decreased the viscosity by <3%.

[4] Evidence for the cyclization of diradicals in cyclic ketone photochemistry has been obtained: H. Wehrli and K. Schaffner, *Helv. Chim. Acta*, **45**, 385 (1962); A. Butenandt and Poschmann, *Ber.*, **77**, 394 (1944); R. L. Alumbegh, G. O. Pritchard, and R. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

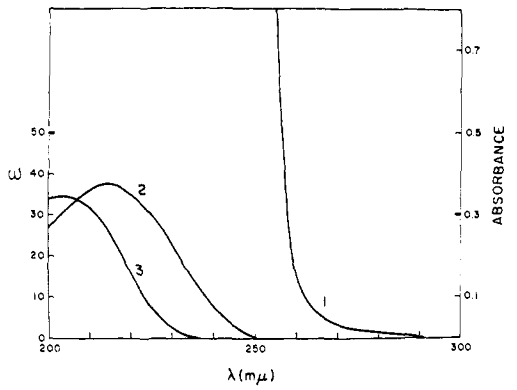

Figure 2. Absorption spectrum of γ-butyrolactone: (1) neat (1 cm path length), ordinate is absorbance; (2) in hexane, ordinate is ε; (3) in water, ordinate is ε.

an increase in the rate of the disproportionation (formation of formate) and fragmentation (formation of cyclopropane) reactions or both.

It has been known for some time that in cyclic ketone photochemistry in solution, products are obtained exclusively from α cleavage of the more substituted bond. Thus, for example, irradiation of methylcyclohexanone gives rise only to *cis*- and *trans*-2-heptenals.[5] Similar results have been noted in steroidal ketones.[6] In the case of lactones, however, the replacement of a hydrogen atom with a methyl group in the γ position does not eliminate or even reduce the carbon–oxygen bond cleavage. This fact is consistent with the conclusion that carbon–oxygen bond fission occurs from a different state than carbon–carbon bond rupture and that this state is the precursor to the triplet state from which carbon–carbon bond fission occurs.[2]

Substitution of a methyl group in the γ position is expected to decrease the yield of the aldehyde product, because only one hydrogen atom is now available for abstraction, but it should not greatly affect the yield of formate. The results are in accord with these expectations. It is probably not worthwhile to speculate here why the yield of cyclopropane product from valerolactone is smaller.

Quenching Experiments. In the earlier study, we found that olefins quenched process 1 and 3 with a bimolecular rate constant that was either diffusion controlled or very close to it, but they did not affect process 2.

From these quenching studies we concluded that (1) monoolefins can be used for the identification of lactone (probably of other simple esters as well) triplet states, and (2) that the lifetime of the excited triplet state can be determined from the Stern–Volmer quenching constant.

The quenching results for valerolocatone show that most, if not all, of the 3-but-2-enyl formate originates from the triplet state. The lifetime of the triplet state of valerolactone is calculated to be 0.7×10^{-9} sec, only about a factor of 2 less than for the triplet state of γ-butyrolactone.

In contrast to the other lactones, the products obtained from α-methylbutyrolactone are not quenched by pentene-2 (1.3 *M*). From this result, it is evident that in this case the formation of the formate may proceed from the singlet state or from a very short-lived triplet state. Since the aldehyde yield was not reduced upon methyl substitution, however, it is more likely that the formate originates from the triplet state.

The decrease in the lifetime of the triplet state on methyl substitution in the γ position is due to an increase in the rate of the excited-state decomposition to formate and cyclopropane rather than to an increase in a radiationless transition to the ground state since the quantum yields of formate and cyclopropane increase. The reason for this increased rate is probably due to a weakening of the α carbon–carbon bond with branching. The evidence for the weakening of carbon–carbon bonds in hydrocarbons with branching is quite convincing, but this is much less so for the α carbon–carbon bond in ketones.[7]

Wavelength Dependence. The increase in the yield of aldehydes (the product obtained by α carbon–oxygen fission) with a decrease in wavelength from 2537 to 2380 Å is a little surprising because both wavelengths lie in the extreme end of the n,π* band, and it appears doubtful that the second transition is excited simultaneously at either wavelength (see Figure 2). For example, the molar absorptivity (ε) for aliphatic ketones at 2100 Å (λ_{max} of high intensity at ~1800, 1700, and 1600 Å)[8] drops to <0.5[9] and at 2400 Å the ε due to the higher energy transitions will be much less. Aliphatic esters also have a high-intensity transition at λ_{max} ~1700 Å[10] and it is probable that the ε at 2400 Å due to this transition will also be very small. In order for absorption due to the second transition to be competitive at 2380 Å, the ε of this transition would have to be ~1–2 (out of a total of 6).

If only the first singlet state is populated at both wavelengths then the most obvious possibility is that the wavelength effect is due to some process occurring from the upper vibrational levels of the first excited singlet state. However, it is usually assumed that vibrational effects in solution will not be important because of the very rapid removal of vibrational energy. Experimental evidence for this assumption, nevertheless, is still sparse, and it appears to us that there is no reason to suppose why some unimolecular decompositions or rearrangements could not be rapid enough to compete with vibrational relaxation.

Stockburger has recently examined the efficiency of vibrational energy transfer from the first singlet state of benzene and naphthalene by a number of foreign gases. His results show that the amount of vibrational energy removed decreases exponentially as a function of the number of collisions. The number of collisions necessary for a decay of ΔE_0 to $\Delta E_0/2.71$ for naphthalene is 33 and 38 for *n*-hexane and benzene as deactivators, respectively, where ΔE_0 is the excess vibrational energy. For the benzene–benzene system, the number of collisions necessary to decrease the vibrational energy by the same fractional amount is 11.[11] Similar results

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[5] R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 2601 (1959).

[6] G. Quinkert, "Organic Photochemistry," International Symposium, Strasbourg, 1964, Butterworth Scientific Publications, London, 1965.

[7] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[8] E. E. Barnes and W. T. Simpson, *J. Chem. Phys.*, **39**, 670 (1963).

[9] W. J. Potts, Jr., *ibid.*, **23**, 65 (1955).

[10] S. Nagakura, K. Kaya, and H. Tsubomura, *J. Mol. Spectry.*, **13**, 1 (1964).

[11] M. Stockburger, International Conference on Photochemistry, Munchen, 1967.

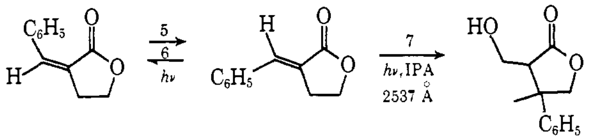
have been obtained earlier by Boudart and Dubois for β-naphthylamine.[12]

If these results can be extrapolated to the condensed phase and to other complex molecules, and if we take the rather liberal range for the number of collisions necessary to reduce the excess energy by 1/2.71 to be from 10 to 100 and the collision frequency in solution as 5×10^{12} sec^{-1},[13] then the vibrational energy relaxation time is in the range of 2×10^{-12} to 2×10^{-11} sec. If the inverse of the first-order rate constant for the excited molecule decomposition is of the same order, then collisional deactivation will compete with chemical reaction.

The upper limit for the singlet-state lifetime in its lowest vibrational level for γ-butyrolactone can be estimated from the quenching of succinaldehyde with biacetyl reported in our previous paper[2] as $\leq 10^{-10}$ sec, indicating very fast rates for the depletion of the singlet state in its lowest vibrational level, and these rates may be even faster for the upper vibrational levels.[14] Thus we see that the singlet-state lifetime approaches the vibrational relaxation lifetime making it a distinct possibility that the two processes are competitive.

The participation of vibrationally excited molecules produced in photochemical systems in solutions has been occasionally invoked by other workers. Thus, for example, Ullman and Henderson have suggested that valance tautomerization of 2,3-diphenylindenone oxide proceeds through a vibrationally excited ground state with a nonrandom distribution of vibrational energy.[15] To make this hypothesis, however, they had to assume that the vibrational relaxation lifetime had the rather large value of $\sim 10^{-10}$ sec.

It is interesting to note that Ullman, Sung, and Baumann have recently observed a wavelength-dependent photochemical reaction in solution for lactones IV and V.[16] They found that reactions 5 and 6 proceed at 3130 and 2537 Å, but reaction 7 occurs only at 2537 Å.



They suggested that the photoreduction reaction 7 proceeds from a $^3(n,\pi^*)$ state and the *cis–trans* isomerization reaction occurs from a $^3(\pi,\pi^*)$ state—the $^3(n,\pi^*)$ state lying above the $^3(\pi,\pi^*)$ state. In their system, one is also confronted with two possible ways of populating the two triplet states: (1) intersystem crossing from different vibronic levels, or (2) intersystem crossing from different singlet states. In this case, alternative 2 appears the favored choice because presumably the ($n \rightarrow \pi^*$) band is buried in the more intense ($\pi \rightarrow \pi^*$) band and at the shorter wavelengths both transitions will be excited.

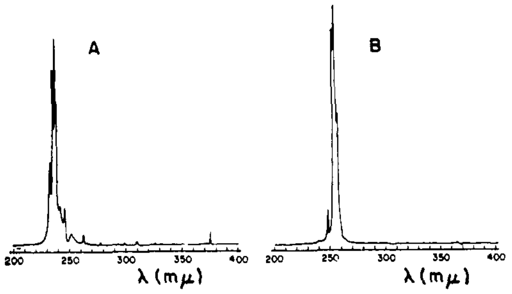


Figure 3. Output of Bausch and Lomb monochromator: (a) monochromator set at 2380 Å, entrance slit 6 mm, exit slit 3 mm; (b) monochromator set at 2540 Å, entrance slit 6 mm, exit slit 3 mm.

Finally, it is worthwhile to note that Ausloos has found that for straight-chain esters in the gas-phase, process 8 occurs at shorter wavelengths than the

$$\mathrm{RCOOR'} \longrightarrow \mathrm{RCO\cdot} + \cdot\mathrm{OR'} \tag{8}$$

process 9.[17] In this case, however, he suggested that a

$$\mathrm{RCOOR'} \longrightarrow \mathrm{R\cdot} + \cdot\mathrm{COOR} \tag{9}$$

different electronic state was populated at the shorter wavelength from which process 8 occurs. The wavelengths used in Ausloos' experiments were shorter than those used by us, and it is quite possible that in his experiments the second transition was excited. However, we feel that in view of our observations, it is more likely that only one transition is excited and that in the vapor phase, process 8 occurs preferentially from upper vibrational levels of the first excited singlet state.

Experimental Section

Materials. γ-Butyrolactone was purified as previously described.[2] Valerolactone (Eastman) and α-methylbutyrolactone (Aldrich) distilled with a spinning-band column at reduced pressure showed absorption in the region 2700–3300 Å. Passage of α-methylbutyrolactone (II) over alumina reduced the absorption in this region to a tolerable level ($A_{2700\,\text{Å}} = 0.08$; neat; 1 cm path length). Valerolactone could not be purified by passage over alumina, and it was found necessary to use a different procedure. Valerolactone (III) was photolyzed in the presence of oxygen with radiation above 3000 Å and distilled. Subsequently, several treatments with large quantities of charcoal virtually eliminated the absorption at 2700 Å.

The absence of absorption at 2700 Å (1 cm path length neat) indicates that the lactones are optically pure. Glpc analysis showed that the remaining impurities which do not absorb in the region >2700 Å were <0.5%.

Pentene-2 (Phillips) was purified by passaged over alumina. The pentene-2 purified in this manner showed no absorption at 2400 Å (10% solution in hexane; 1 cm path length), and glpc showed the presence of only a trace of pentene-1.

Apparatus and Methods of Analysis. The neat lactones were irradiated in a cylindrical Cary cell with light from a Hanovia medium-pressure lamp rendered monochromatic with a Bausch and Lomb monochromator (64 Å/mm). The output of this monochromator for wavelength settings of 2537 and 2380 Å as analyzed by a second monochromator is shown in Figure 3. The relative height of the lines is their relative intensity, since the light output of the second monochromator was detected by a photomultiplier tube in front of which a sodium salicylate screen was placed. It is known that the fluorescence yield of sodium salicylate is independent of wavelength from 1000 to 3000 Å.[18]

For the determination of quantum yields as a function of wavelength, the relative light intensity was measured with a sodium

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(12) M. Boudart and J. T. Dubois, *J. Chem. Phys.*, **23**, 223 (1955).

(13) D. F. Eggers, *et al.*, "Physical Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964.

(14) In this connection it is interesting that rate constants for intersystem crossing and internal conversions for cyclobutanone in the vapor phase have been estimated to be $>10^{11}$ sec^{-1}: N. E. Lee, H. V. Denschlag, and E. K. C. Lee, to be published. We are indebted to E. K. C. Lee for a preprint of their paper prior to publication.

(15) E. F. Ullman and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **88**, 4942 (1966).

(16) N. Baumann, M.-t. Sung, and E. F. Ullman, *ibid.*, in press. We thank the authors for a preprint of their paper.

(17) P. Ausloos, *Can. J. Chem.*, **36**, 383 (1958).

(18) H. Inokuchi, Y. Harada, and T. Kondow, *J. Opt. Soc. Am.*, **54**, 842 (1964).

salicylate coated RCA 935 phototube. The relative quantum yields were calculated from

$$\frac{\Phi_{2537}}{\Phi_{2380}} = \left(\frac{A_{2537}}{A_{2380}}\right)\left(\frac{(R_o - R_e)_{2380}}{(R_o - R_e)_{2537}}\right)\left(\frac{t_{2380}}{t_{2537}}\right)$$

where A is the chromatogram area, R_o and R_e are the phototube readings when the cell is filled with water and with lactone, respectively, and t is the time of irradiation. The absolute quantum yield at 2380 Å was then obtained from the known absolute quantum yields at 2537 Å.

The formates were identified by comparison of their retention times and infrared spectra with authentic samples. In the case of crotyl formate, the spectra of the known and unknown sample were identical, except that the unknown sample exhibited a band at 849 cm^{-1}, but the known sample did not show this band. Since the band at 849 cm^{-1} is characteristic of a carbon–hydrogen bending mode for *cis* olefins, it was concluded the unknown sample was a mixture of the *cis* and *trans* isomers, whereas the known sample was the *trans* isomer. Complete separation of the two isomers by glpc was not achieved, but with a benzylcyanide–$AgNO_3$ column, it was possible to partially resolve the single peak appearing on a Carbowax 20M column into one peak with a shoulder.

Succinaldehyde was identified by comparison of its infrared spectrum to that reported in the literature and by comparison of the retention time to that of an authentic sample. In addition, the photoproducts of the unknown material were identical with those of independently synthesized succinaldehyde. α-Methylsuccinaldehyde was identified by its infrared spectrum and retention time.

A sufficient amount of the product obtained from valerolactone, with a retention time close to the aldehydes obtained from the other lactones, could not be obtained for infrared analysis and its identity is not certain. However, by analogy with the formation of the dialdehydes from butyrolactone and α-methylbutyrolactone and from the similarity of the retention time of this compound to those of the dialdehydes, it is probably pentanal-4-one.

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Mechanism of Ketene Formation from Cyclohexenones upon Electron Impact. Correlations with Photochemistry[1]

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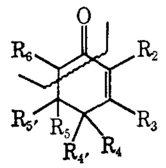
Abstract: The high-resolution mass spectra and the metastable ions of a number of alkyl-substituted 2-cyclohexenones and related bicyclic and steroidal unsaturated ketones, together with deuterium-labeled analogs, have been measured and the course and the scope of electron impact induced rearrangements and fragmentations occurring in these compounds discussed. A similar study of alkyl-substituted bicyclo[3.1.0]hexan-2-ones, derived from the cyclohexenones by photochemical transformation, is reported. A variety of data support the postulate that on electron impact, a portion of the molecular ions of 2-cyclohexenones rearrange to molecular ions resembling those formed from related bicyclo[3.1.0]hexan-2-ones, and it is from these rearranged ions that ketene is eliminated.

The elimination upon electron impact of the elements of ketene from various cyclohexenones[3,4] and from cyclohexenone systems in steroids[5–8] and 2-octalones[9,10] has been frequently observed. The identity and the origin of the atoms lost have been confirmed by isotope labeling and exact mass measurements[3–11] and the elimination is shown, at least formally, below.



The loss of ketene, as indicated, requires the scission of a vinylic bond. It has been shown in a number of cases that cleavage of such a bond is severely repressed or inoperative when compared to scission of the corresponding σ bond in the saturated analog.[12–15] Since ketene elimination is rarely seen in the fragmentation of saturated six-ring ketones,[16–18] it seems unlikely that

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