maximum σ-overlap of the p-orbitals. The HMO calculated ground-state energy lowering for IIa is equivalent to *ca.* 6 kcal./mole (β = 18 kcal./mole), whereas II, in a noncrown conformation, is expected to possess no D.E. Therefore, it is necessary to determine the conformation of II in order to gain information about any added stabilization due to π-electron delocalization.

Evidence favors a noncrown conformation. The melting point, −1.5°, seems low for II to have C_{3v} symmetry in comparison to I (m.p. 50°) and III (m.p. 34°). The ultraviolet spectrum of II showed only end absorption, unlike I, which has been proved to be in a crown conformation.[1c,1f] The dipole moment of VIII was found to be 0.6 D., showing that VIII is not in a crown conformation (a calculated dipole moment for VIII in a crown conformation is >3 D.). The magnitude of the vicinal coupling constants[6] for the ethano hydrogens of VIII (which is interconverting between equivalent conformers) strongly favors an *s-trans* arrangement. Molecular models show that IIc is less strained than IId and, in addition, that the bromines in VIII would cause no serious steric interactions in the various conformations considered.

Though the conformation of II is not proved, we conclude from these data that II is in a noncrown conformation and that its actual conformation is likely to be IIc. The conclusion that II is in a noncrown conformation, however, does not allow the inference that σ-overlap of the p-orbitals of a different cyclic π-electron system will be completely ineffective at lowering its ground-state energy. The conformer IIa, with C_{3v} symmetry, contains six pairs of eclipsed ethano hydrogens which alone could raise its energy by as much as 6 kcal./mole due to nonbonded interactions. Thus, any stabilization IIa may gain from π-electron delocalization is outweighed by its nonbonded interactions.

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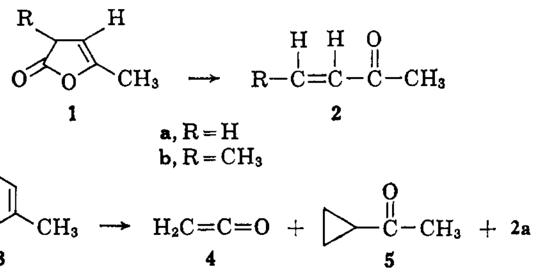
Irradiation of Enol Lactones

Sir:

We have recently reported on the irradiation of enol benzoates,[1] enol acetates,[2] and dienol acetates[3] by a low pressure mercury lamp. We wish now to report the extension of this study to include photochemistry of enol lactones by the same light source.

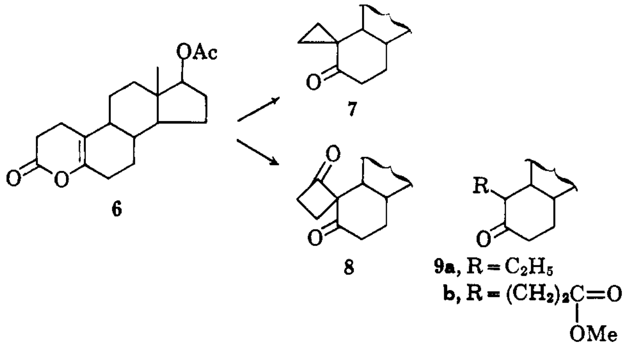
When angelica lactone (**1a**) was irradiated in pentane solution for 6 hr., it was converted in 30% yield to methyl vinyl ketone (**2a**), which could be obtained in pure form *via* direct distillation of the pentane solution. The residue consisted of unchanged starting lactone **1a**. No additional products could be detected by g.l.c. separation, and the n.m.r. spectrum of the total irradiated solution showed the signals due to **1a** and **2a** only. When the irradiations of **1a** were carried out in *t*-butyl alcohol or methanol for similar periods of time, no significant changes in the yield were found. Similarly the enol lactone **1b**[4,5] was converted in 40% to propenyl methyl ketone (**2b**) after 4 hr. irradiation.

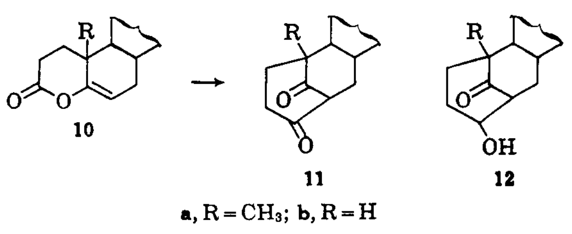
Photolysis of the six-membered enol lactone **3**[6] for 7 hr. resulted in the formation of ketene (**4**), methyl cyclopropyl ketone (**5**, 18%), and methyl vinyl ketone (**2a**, 7%); 60% of the starting lactone could be also recovered. The ketene was trapped in pentane solution by a low temperature distillation, and the other two products were separated by fractional distillation.



Irradiation of analogous steroidal lactones **6**[7] for 20 min. resulted in *ca.* 50% conversion. The main product was the cyclopropyl ketone **7** (40%). In addition small amounts of cyclobutanone product **8** (3%) and a dimeric ketone $C_{34}H_{50}O_7$ (2%) were isolated. The structure of the cyclopropyl ketone **7** was deducted from its physical properties[5] and its reduction with zinc and acetic acid to the α-ethyl ketone **9a**, and that of cyclobutanone product **8**[5] from its ready methanolysis to the keto ester **9b**.

Irradiation of the exocyclic enol lactone **10a**[8] for 18 hr. resulted in the non-enolic diketone **11a** (15%; recovered starting lactone 50%). Its structure was established by a direct comparison with chromic acid





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[1] M. Gorodetsky and Y. Mazur, *Tetrahedron Letters*, 369 (1963).

[2] A. Yogev, M. Gorodetsky, and Y. Mazur, *J. Am. Chem. Soc.*, **86**, 5208 (1964).

[3] M. Gorodetsky and Y. Mazur, *ibid.*, **86**, 5213 (1964).

[4] Prepared from 2-methyl-4-ketopentanoic acid.

[5] Satisfactory elemental analyses and compatible ultraviolet, infrared, and n.m.r. spectra were obtained for all new compounds.

[6] D. Vorländer and A. Knötzsch, *Ann.*, **294**, 317 (1897).

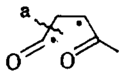
[7] J. A. Hartman, A. J. Tomasewski, and A. S. Dreiding, *J. Am. Chem. Soc.*, **78**, 5662 (1956).

[8] G. I. Fujimoto, *ibid.*, **73**, 1856 (1951); H. J. Ringold and G. Rosenkrantz, *J. Org. Chem.*, **22**, 602 (1957).

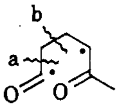
oxidation product of the ketol **12a**.[9] The corresponding enol lactone **10b**[8] afforded the diketone **11b**. Since the latter could not be isolated in pure form it was hydrogenated over platinum oxide to yield, *inter alia*, the ketol **12b**.[9]

The results of the irradiations of the enol lactones can be explained by assuming a primary cleavage of the carbonyl oxygen bond forming a diradical intermediate i, ii, or iii, respectively (mesomeric with the corresponding enol radicals). This cleavage is analogous to the one previously postulated in the conversion of enol esters.[1-3] The intermediate diradicals can be stabilized by: (i) direct recombination of the carbonyl radical with the "α-keto radical" to give a diketone; (ii) loss of carbon monoxide from the carbonyl part of the diradical and formation of a ring or double bond with the vinylic carbon atom (fragmentation a); (iii) cleavage of the C–C bond β to the carbonyl radical (fragmentation b).

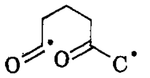
The six-membered lactones with the exocyclic double bond give on photolysis products derived by process i only, and the five-membered endocyclic lactones products by process ii only. Since these enol lactones are readily obtained from the corresponding keto acids, the irradiation of both types of lactones can be used as a convenient synthetic route for the preparation of the corresponding bridged diketones and vinyl ketones. The irradiation of the six-membered endocyclic enol lactones afforded products derived by all three processes. Although no α-acetylcyclobutanone could be identified among the irradiation product of **3**, a coloration with ferric chloride solution was observed in the total reaction mixture which could indicate the formation of this derivative. On the other hand, the dimeric material isolated from irradiation of **8** could be an artifact resulting from dimerization of the α-methylene ketone[10] obtained by loss of ketene from **6**.



i



ii



iii

It seems that the cleavage of the enol lactones to a diradical intermediate is the preferred one when irradiated by a comparatively low wave length light. On the other hand, a related reversible photoconversion of non-enolic cyclohexane-1,3-diones to the exocyclic enol lactones has recently been reported using a longer wave length source.[11] It is pertinent to mention that the enol lactones show electronic transitions at λ_{max} 230–245 mμ,[12] not far from the main wave length emitted by the low pressure mercury lamp (254 mμ) used in the experiments described here.

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[9] The ketols **12a** and **12b** were obtained by lithium tri-*t*-butoxyaluminum hydride reductions of the corresponding enol lactones **10a** and **10b**, respectively; to be published later. *Cf.* J. Martin, W. Parker, and R. A. Raphael, *J. Chem. Soc.*, 289 (1964).

[10] Dimerization of analogous α-methylene ketones is well known; *cf.* E. Romann, A. J. Frey, P. A. Stadler, and A. Eschenmoser, *Helv. Chim. Acta*, **40**, 1900 (1957).

[11] H. Nozaki, Z. Yamaguti, and R. Noyori, *Tetrahedron Letters*, 37 (1965); R. C. Cookson, A. G. Edwards, J. Hudec, and M. Kingsland, *Chem. Commun.*, 98 (1965).

[12] These transitions are seen in the o.r.d. and c.d. curves of the optically active enol lactones; to be published later. *Cf.* H. Wolf, *Tetrahedron Letters*, 1075 (1965).

[13] Taken in part from the Ph.D. thesis submitted to the Scientific Council of the Weizmann Institute of Science.

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γ-Radiation-Induced Exchange of Deuterium with Silica Surfaces[1]

Sir:

A recent article describing the radiolysis of azoethane adsorbed on silica gel and magnesium oxide implied a certain model for γ-ray energy transfer phenomena.[2] Very briefly, radiation-produced excitations in the solid are assumed to migrate rather large distances, during which time volume defects compete with surface states for the excitation energy. It was interesting to see whether this model could apply to the direct isotopic exchange radiolysis of silica gel[3a]

$$SiO_{3/2}OH + D_2 \rightsquigarrow SiO_{3/2}OD + HD^{3b} \qquad (1)$$

In particular, the variation of the HD yield as a function of crystal form, dose rate, purity, and particle size or surface area might reveal how far and how well the radiation energy could migrate.

The experimental techniques were similar to those described.[3a] Three low-area silicas, α-cristobalite, vitreous silica, and quartz,[4] were prepared by grinding appropriate materials. Silica gel of reduced surface area was prepared from Fisher silica gel by steaming or treating with ammonia. Surface areas were determined by N_2 adsorption and are given in Table I, column 2. Samples were degassed overnight at 410° before the first irradiation and annealed at 350° between irradiations. Samples were irradiated with ^{60}Co γ-rays or 2-Mev. Van de Graaff electrons to doses of 0.5 to 3 × 10^{20} e.v./g. and at dose rates varying from 10^{18} to 3 × 10^{21} e.v./g. min. H_2, HD, and D_2 were determined gas chromatographically.[5] Since there was considerable overlap of the H_2 and HD peaks, the gel was not deuterated as in ref. 3a; rather deuterium reacted with the protium gel. The 100-e.v. yields of exchangeable surface hydrogen at lowest dose rates based on energy absorbed in the total system are given in Table I, column 4. As the dose rate increased, the yield dropped monotonically to about two-thirds of the low dose rate value.

The 100-e.v. yields cited in Table I, column 4, assume that all the energy deposited in the solid is equally effective in causing reaction of the surface. A more reasonable assumption would be that only the energy

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] J. G. Rabe, R. Rabe, and A. O. Allen, *J. Am. Chem. Soc.*, **86**, 3887 (1964).

[3] (a) H. W. Kohn, *J. Phys. Chem.*, **66**, 1017 (1962). (b) This formula was used in ref. 3a. A more exact formulation would be $SiO_x(OH)_y + yD_2 \rightsquigarrow SiO_x(OD)_y + yHD$, where x and y depend on conditions of degassing. This reaction is of course followed by $2HD \rightleftharpoons H_2 + D_2$.

[4] Mrs. Eleanor Pomerance of Oak Ridge and Vienna donated the oscillator-grade Brazillian quartz from her private collection.

[5] W. R. Moore and H. R. Ward, *J. Phys. Chem.*, **64**, 832 (1960).