

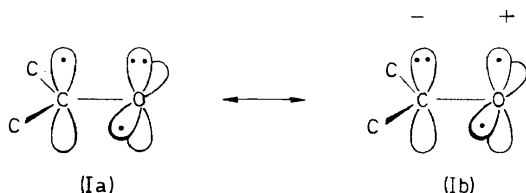
# CYCLIC KETONES: PHOTOLYTIC ELIMINATIONS AND REDUCTIONS

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## INTRODUCTION

The atomic orbital resonance model (I a)  $\longleftrightarrow$  (I b) of the  $n, \pi^*$  excited carbonyl group suggests that, on one hand, both carbonyl oxygen and carbon should possess radical-like reactivities and, on the other hand, the oxygen should approach the chemical properties of an electrophilic and the carbon those of a nucleophilic site. This frequently quoted, simple concept has served as a useful illustration of the major primary processes which prevail in the solution photochemistry on non-conjugated ketones. A serious restriction of its predictive value for many cases, however, derives from its failure to correlate reactivity with additional, partly inter-dependent



features of the excited states with  $n, \pi^*$  configuration which could modify these models in chemically significant ways. Excited carbonyl singlet and triplet  $n, \pi^*$  states may exhibit notably different inherent reactivities. Other aspects that will require future attention are, e.g., the extent to which the non-bonding  $p_y$  orbital is delocalized in the reactive species, and the nuclear geometry of equilibrated  $n, \pi^*$  ketone singlets and triplets. Thus, formaldehyde is known<sup>1</sup> to adopt pyramidal forms. For ketones one may expect a similar situation which could bear particularly on the steric requirements for intramolecular interactions with rigidly oriented reaction sites.

## PHOTOLYTIC CLEAVAGE

One major class of ketone reactions referred to above is the light-induced cleavage of bonds attaching suitable atoms or groups to the  $\alpha$ -carbon of ketones in processes other than the type II-cycloeliminations. It is widely documented in the literature for a considerable number of examples  $X-C_\alpha-C=O$  with  $X$  = mostly electronegative substituents or cyclopropane carbons. On the basis of the resonance representation (I a, b) the  $n, \pi^*$  carbonyl had been assigned the dual capacity of ejecting such substituents as either radicals or anions<sup>2</sup>. Here again, efficiency and detailed mode of the cleavage process may critically depend not solely on the nature

of X and the medium, but also on the spatial orientation of the departing group. It has been pointed out recently<sup>3</sup> that the effect of  $\alpha$ -substituents on the absorption energy and intensity of the keto group should be largely due to  $\sigma^*_{C_\alpha-X}$ ,  $\pi^*$  interactions. The size of this effect will be determined therefore by both the energy of the perturbed  $\sigma^*$  orbital of the  $C_\alpha-X$  bond and its orientation with respect to the keto group, and so will be at the same time the extent to which  $C_\alpha-X$  bond cleavage will be facilitated already in the respective excited state. A very familiar illustration of this situation is exemplified by  $\alpha$ -halogenated cyclohexanones where the axial, but not the equatorial halogen, causes an increase in wavelength and intensity of the  $n \rightarrow \pi^*$  ketone transition. A stereochemical control which would be in accord with the steric requirement of a  $\sigma^*$ ,  $\pi^*$  assisted elimination, has been reported<sup>4</sup>: Photolytic cleavage of the  $C_\alpha-N$  bond in a cyclohexanone system with an axial  $\alpha$ -dimethylamino group was achieved while in the isomer with the  $\alpha$ -substituent in the equatorial position no photodeamination occurred.

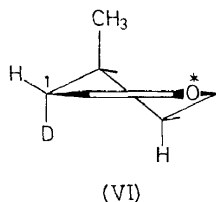
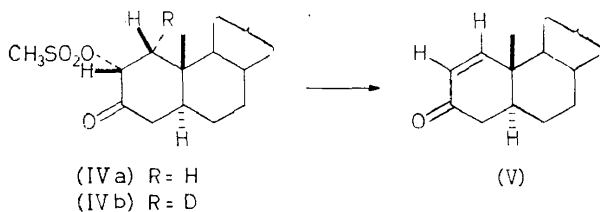
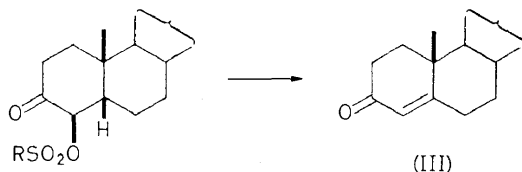
Our own efforts in this area of ketone reactivity have centred primarily on  $\alpha$ -sulphonyloxyketones and  $\alpha,\beta$ -epoxyketones. Both compound types undergo transformations which involve  $C_\alpha-O$  cleavage and, in many cases, result in sufficiently high chemical yields to suggest the respective photo-reactions as potent synthetic tools of wide applicability<sup>†</sup>. When the steroidal sulphonyloxyketones (II a), (II b), and (IV a) were irradiated in benzene solutions with wavelengths  $>310 m\mu$ , elimination of sulphonic acid and formation of the corresponding  $\alpha,\beta$ -unsaturated ketones (III and V, respectively) occurred as the virtually exclusive chemical change. The  $1\alpha$ -deuterated compound (IV b) yielded product (V) as well. The selective loss of deuterium from (IV b) locates precisely the origin of the elements eliminated. Although no further conclusions with regard to the detailed course of the reaction are possible, this observation is perhaps best understood if a stepwise elimination sequence is assumed with a stereoelectrically controlled expulsion of either  $D\cdot$  or  $D^+$  from a primary photoproduct of type (VI, \* =  $\cdot$  or  $+$ ). A concerted process of cycloelimination of  $CH_3SO_3H(D)$  is a possible alternative but would be expected to be less stereoselective with regard to the attack at C-1 of (IV b).

The monocyclic (VII) and the aliphatic sulphonyloxyketones (X a,b) were chosen next. Elimination of sulphonic acid from these compounds would, for structural reasons, demand skeletal rearrangements. This was indeed the case: irradiation ( $>310 m\mu$ ) of (VII) in benzene gave a mixture of the rearranged cyclohexenone (VIII) as the major component, and the saturated ketone (IX). The formation of the latter product (IX) increased relative to the rearrangement to (VIII) when appropriate hydrogen donors, e.g. triethylamine, were added. But we note that either hydrogen abstraction by the carbonyl oxygen or expulsion of the mesyloxy group are available as the photochemical step in this reductive elimination reaction. The formation of the  $\alpha,\beta$ -unsaturated ketone (VIII) is only compatible with a sequence of  $C_\alpha-O$  fission and 1,2-methyl migration, and it rules out in particular a cyclic process of sulphonic acid elimination. The aliphatic

<sup>†</sup> Part of the results presented here have been reported previously; cf. references 5, 6, and 18, and the literature cited therein.

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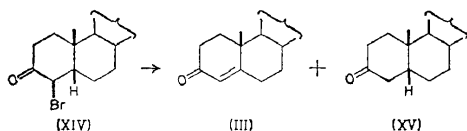
compounds (X a) and (X b) were subjected to a similar 1,2- methyl shift upon photoelimination, leading to ketone (XI) as the major product of the photolyses. Intervention of external hydrogen donors was at best negligible here. The  $\alpha$ -hydrogens of three methyl groups provided an intramolecular abstraction site instead, giving rise to four additional isomers (XII, a,b and XIII a,b). The sequence of events—attack at CH<sub>3</sub>-6, elimination of the sulphonyloxy group, and rearrangement—in these transformations remains to be determined. The ratio of the five products, (XI),



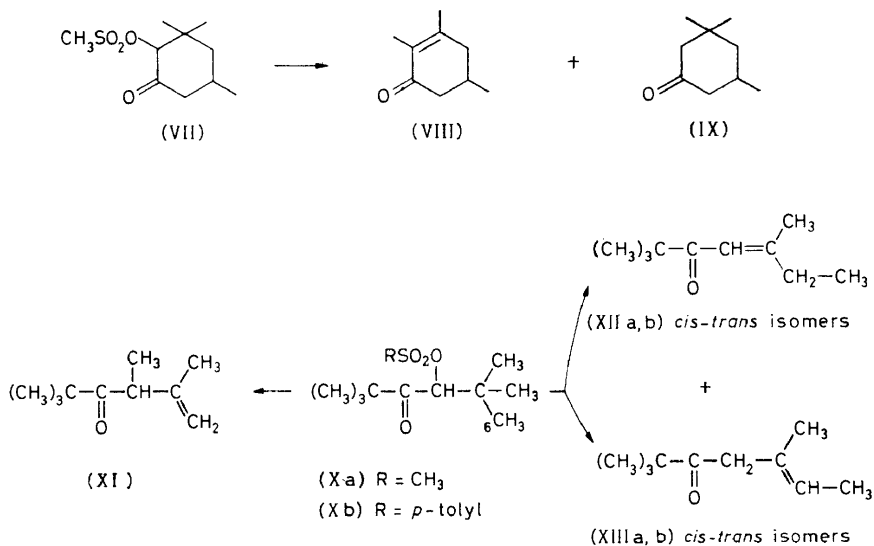
(XII a,b), and (XIII a,b), remained constant during the photolyses of (X a) and (X b), excluding thus the possibility that the  $\beta,\gamma$ -unsaturated ketones (XI) and (XIII a,b) arise from light-induced double bond migrations of conjugated precursors (e.g., XII  $\rightarrow$  XIII).

As demonstrated particularly by the cyclic compounds (II), (IV), and (VII), photolysis may offer a convenient preparative method to degrade  $\alpha$ -sulphonyloxyketones to conjugated enones<sup>†</sup>. Competitive photoreactions

<sup>†</sup> Photochemical eliminations of this general type are not restricted to  $\alpha$ -sulphonyloxyketones, but are also observed, e.g., with  $\alpha$ -bromoketones. Thus, photolysis of (XIV) in dioxane, a fairly good hydrogen donating solvent, led to approximately equal amounts of (III) and (XV).



of starting materials and products can either be prevented by a choice of appropriate reaction conditions (to avoid bimolecular reductions,



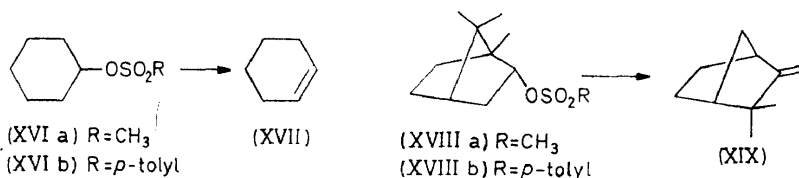
cyclodimerizations) or are too inefficient to interfere notably (cyclohexenone  $\rightarrow$  bicyclo[3.1.0]hexanone rearrangement).

Attention to three mechanistic considerations are in order at this point: first, the dihedral angle between the C=O and the C $_{\alpha}$ -O bonds should greatly differ in the cyclic ketones of type (II), (IV), and (VII) on one hand, and in (X) on the other. While these bonds are practically eclipsed in the former group of compounds, they are likely to adopt a relatively large angle in (X) in order to minimize steric repulsion between the bulky *tert*-butyl groups. The difference is reflected in the  $n \rightarrow \pi^*$  absorption maxima which are shifted towards longer wavelengths in the aliphatic ketones (312  $m\mu$ ) than in the cyclic compounds (290–298  $m\mu$ ). Yet, the photochemical results of direct irradiation do not seem to differ qualitatively. A difference which cannot be evaluated satisfactorily yet is that the transformations of the cyclic sulphonyloxyketones, as described above, were also effected by benzene sensitization (irradiation of benzene solutions with wavelength 253.7  $m\mu$ ), whereas the aliphatic compounds remained unchanged under these conditions.

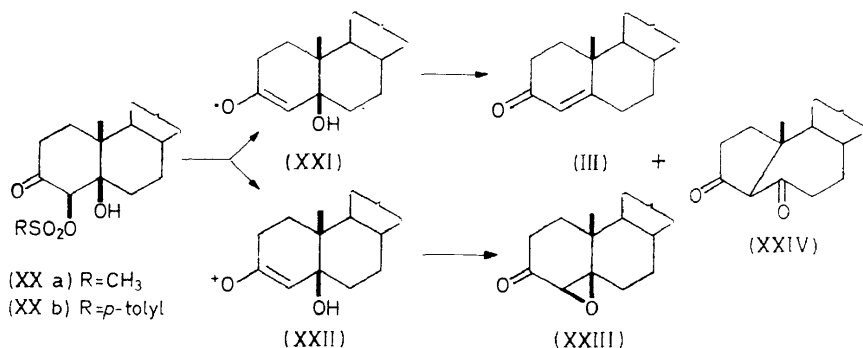
Another question concerns the possibility that RSO<sub>3</sub>H elimination from the  $\alpha$ -sulphonyloxyketones is preceded by a transfer of excitation energy from the carbonyl to the sulphonate group rather than it is initiated by a photochemical cleavage originating directly from the excited keto group itself. In order to test such a variation from the elimination mechanism(s) referred to at the beginning, acetone sensitization of cyclohexyl mesylate (XVI a) was attempted. While no chemical change of (XVI a) could be detected under

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these conditions, the formation of olefins, cyclohexene (XVII) and camphene (XIX), respectively, was observed with the alkyl sulphonates (XVI a,b) and (XVIII a,b) in benzene solutions with 253.7 m $\mu$ -irradiation. Direct excitation of the cyclohexyl (XVI b) and bornyl tosylates (XVIII b) in *tert*-butanol with light of 253.7 m $\mu$  gave again the corresponding olefins, (XVII) and (XIX). Comparative runs with (XVI a,b), (XVIII a,b), and (VII) indicated, however, that the elimination from the alkyl sulphonates are distinctly less efficient than that from the sulphonyloxyketones. A chemical participation of the excited carbonyl group in the photolytic degradation of the latter appears more likely from these results than an intramolecular energy transfer to the sulphonate moiety.



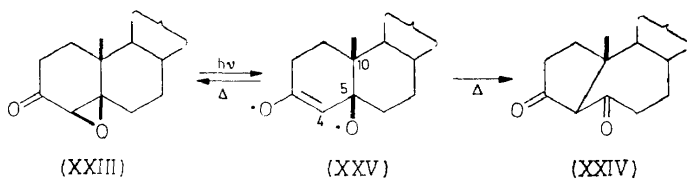
Finally, in an attempt to differentiate between a homolytic and a heterolytic mode of sulphonyloxyketone photocleavage, compounds (XX a,b) were photolyzed in benzene solutions. Upon both direct excitation with wavelengths  $>310$  m $\mu$  and solvent sensitization using 253.7 m $\mu$ -light the resulting photoproduct patterns were the same, consisting of components (III), (XXIII), and (XXIV). The structure of these compounds renders a single primary photoproduct as the common precursor unlikely. It appears rather more plausible to assume that two different cleavage processes operate parallel—a homolytic dissociation of the C $_{\alpha}$ —O bond ( $\rightarrow$  XXI) and a heterolytic fission to (XXII). Thus elimination of HO $\cdot$  from radical (XXI) and cyclization and deprotonation of the cationic species (XXII) seem rational secondary reactions to lead to the  $\alpha,\beta$ -unsaturated ketone (III) and the  $\alpha,\beta$ -epoxyketone (XXIII), respectively. Alternative cleavage modes such as elimination of HO $^{+}$  from (XXII) ( $\rightarrow$  III) and homolytic fission of the



O—H bond in (XXI) ( $\rightarrow$  XXIII) are clearly less favourable. The third product formed in these irradiation experiments, (XXIV), may result either from rearrangement of the primary product (XXII) or from photoisomerization of the epoxyketone (XXIII).

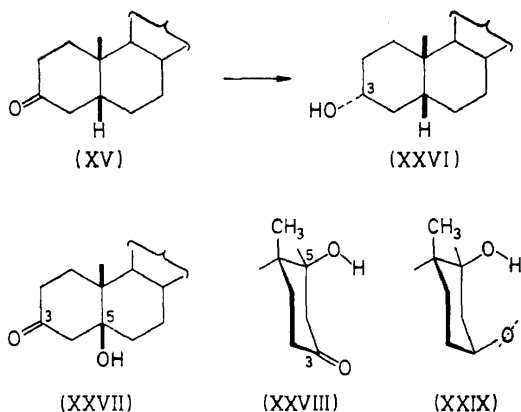
### PHOTOLYTIC REDUCTIONS

The photorearrangement of  $\alpha,\beta$ -epoxyketones to  $\beta$ -dicarbonyl products (cf. XXIII  $\rightarrow$  XXIV)<sup>7</sup> constitutes another example which has been proposed to proceed *via* light-induced C $_{\alpha}$ —O cleavage. The diradical character of the resulting primary product (XXV) had been assigned on the basis of migrational aptitudes of various  $\beta$ -groups (C-10 in XXV) in the subsequent rearrangement step<sup>6,8-10</sup> [C-10(5 $\rightarrow$ 4) migration in XXV  $\rightarrow$  XXIV] which competes with oxirane reclosure. The experiments discussed below had been initiated to investigate the 'possibility of intercepting the proposed primary photoproduct (XXV) using a highly efficient hydrogen donor, tri-*n*-butylstannane. In order to achieve this goal reaction conditions had to be explored which would prevent photolytic abstraction of stannane hydrogen by the epoxyketone, but would not interfere with the primary photochemical step leading to rearrangement. Both processes could *a priori* be expected to yield the same hydroxyketone (XXVII) after the incorporation of two hydrogens or, eventually, the corresponding 3 $\xi$ ,5 $\beta$ -dihydroxy derivatives after further photoreduction. Since the epoxyketone rearrangement (XXIII)  $\rightarrow$  (XXIV) was observed also in neat 1,3-pentadiene which does not affect reactions of singlet excited saturated ketones but quenches triplet processes<sup>11</sup>, we turned first to investigate the singlet excited state reactivity of the parent non-substituted ketone (XV) towards bimolecular reduction. Irradiation ( $>310\text{ m}\mu$ ) of 0.03 M solutions of (XV) both in isopropanol and in benzene containing 0.74 M tri-*n*-butylstannane resulted likewise in the expected reduction as the only photochemical transformation, yielding the 3 $\alpha$ -hydroxy compound (XXVI).



However, similar concentrations of (XV) in 1,3-pentadiene solutions containing 5.7 M isopropanol and 0.74 M stannane, respectively, remained photostable. The result documents that hydrogen abstraction by singlet excited ketone cannot be enforced even by high concentrations of the very reactive stannane<sup>12</sup> under these conditions $\dagger$ .

$\dagger$  Recent reports in the literature parallel some of our own findings. Markos and Reusch<sup>8</sup> found no effect of diene triplet quenchers on the rearrangement of isophorone epoxide. They conclude that the photolytic oxide fission (cf. XXIII  $\rightarrow$  XXV) occurs predominantly from the singlet excited state of the epoxyketone. Furthermore, Wagner<sup>13</sup> observed complete inhibition of acetone photoreduction by tri-*n*-butylstannane in the presence of diene triplet quenchers and suggests that the excited singlet acetone is much less reactive than the triplet.

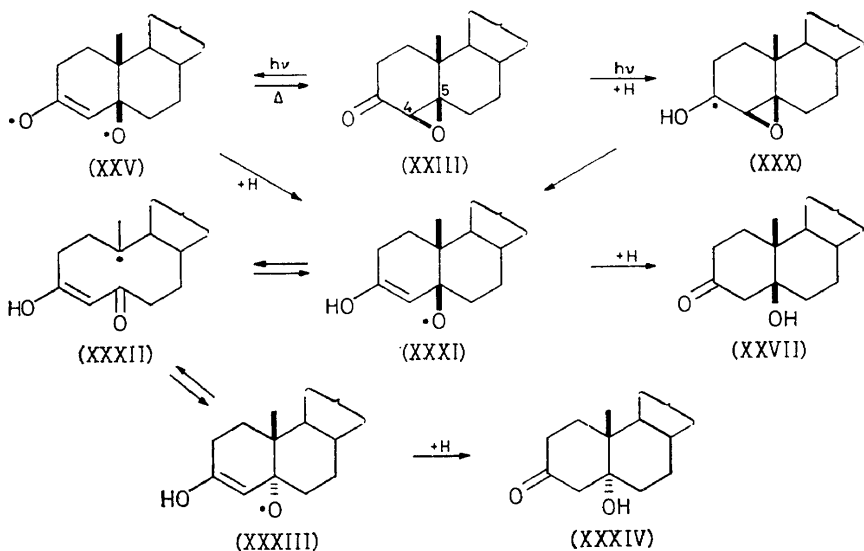


Interestingly, the photoreduction of the hydroxyketone (XXVII) by stannane in benzene proved to be markedly less efficient than the reduction of ketone (XV) in comparable runs, whereas in isopropanol solutions the photochemical hydrogen abstraction capacities of (XV) and (XXVII) were about equal. Apparently the angular hydroxyl group in (XXVII) provides a pathway to reduce the reactivity of the excited carbonyl group in benzene. In isopropanol, however, where the hydroxylic hydrogen interacts strongly with the solvent, this effect is absent. Hydroxyl and keto groups are sufficiently separated in (VII) to exclude intramolecular hydrogen bonding of the type  $\text{—OH} \cdots \text{O}=\text{C}$ . Before more experimental data are available, an evaluation of this result will remain speculative. The reduced efficiency of intermolecular hydrogen abstraction is somewhat reminiscent of, e.g., the *o*-hydroxy- and *o*-methylbenzophenones which fail to undergo net photochemical changes<sup>14</sup>. The hydrogens of the *ortho* substituents are suitably placed in these compounds for transfer to the carbonyl oxygen through a six-membered cyclic transition state, resulting in a reversible 'photoenolization'. In ground state molecular models of (XXVII) the steric requirements for the transition state of such a hydrogen transfer are less satisfactory (cf. XXVIII). However, it should be noted that, if the  $n, \pi^*$  excited keto group should assume a pyramidal geometry, the electron-deficient non-bonding  $p_y$  orbital on the oxygen would approach the hydroxylic hydrogen in one of the two possible orientations (cf. XXIX). This may suffice for an association and hence provide a pathway for energy dissipation without entirely breaking the O—H bond. A complete hydrogen transfer would be energetically less favourable than in the *ortho* substituted benzophenones and should, moreover, lead in part to an unobserved irreversible type II fragmentation.

Since the photoreduction of ketone (XV) by stannane is quenched completely while the epoxyketone rearrangement (XXIII)  $\rightarrow$  (XXIV) still occurs upon irradiation in 1,3-pentadiene solutions, hydrogen addition to the proposed primary photoproduct of the epoxyketone seemed a feasible objective. Surprisingly, however, irradiation of a 1,3-pentadiene solution containing 0.03 M epoxyketone (XXIII) and 0.74 M tri-*n*-butylstannane

with wavelengths  $>310\text{ m}\mu$  produced no observable chemical change of (XXIII). No rationale of this unexpected photostability of the epoxyketone (XXIII) in the pentadiene-stannane system is yet seen, and its investigation is pursued further.

In benzene solution with the same concentrations of epoxyketone (XXIII) and stannane as in the preceding experiment, irradiation ( $> 310\text{ m}\mu$ ) gave no rearrangement to (XXIV) but a more rapid transformation to a mixture containing the  $5\beta$ -hydroxyketone (XXVII) and its  $5\alpha$ -stereoisomer (XXXIV) in the approximate ratio 6:1. The greater rate of epoxyketone conversion and the lack of  $\beta$ -diketone (XXIV) formation may indicate that hydrogen addition from stannane to the primary photoproduct (XXV) competes more favourably with oxirane reclosure than does the rearrangement to (XXIV). However, an equally compatible route to the hydroxyketones is available in the photolytic hydrogen abstraction by the epoxyketone carbonyl (XXIII  $\rightarrow$  XXX) if this process is more efficient than the  $C_\alpha$ -O fission (XXIII  $\rightarrow$  XXV). A differentiation between the two mechanisms is not possible at this stage. The formation of the two stereoisomeric hydroxyketones (XXVII) and (XXXIV) requires that in the stepwise hydrogen addition in either mechanistic alternative at least to some extent the inter-



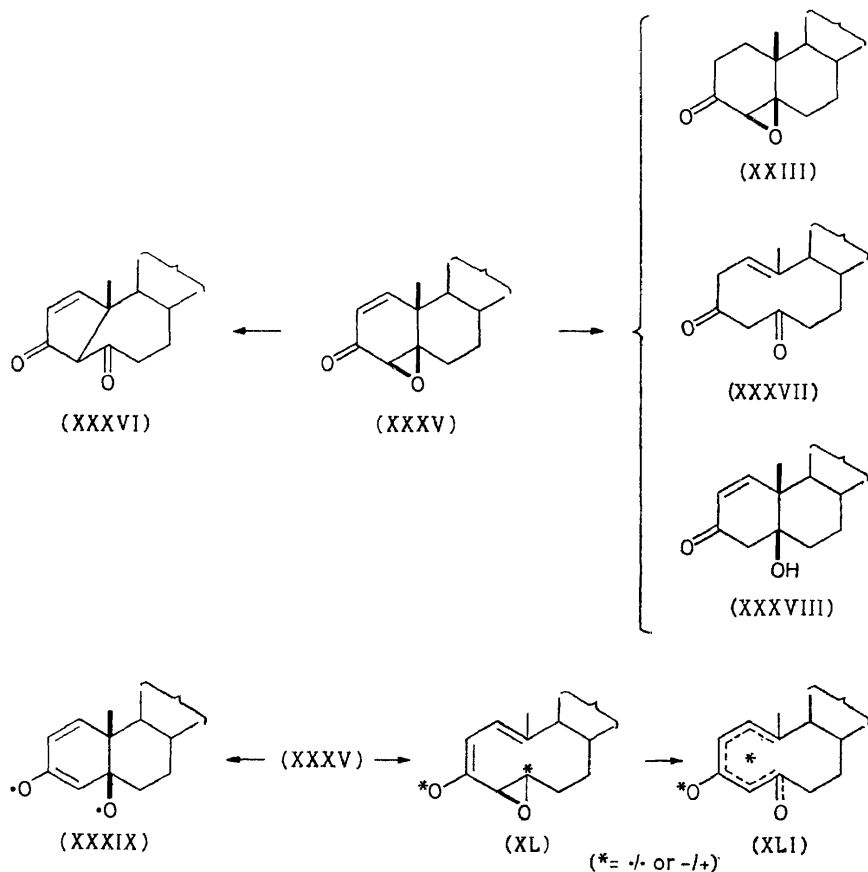
mediate (XXXI) (or its 3-keto tautomer) is produced which can epimerize to (XXXIII) through the fragmented species (XXXII). The reversibility of this process is apparent from the photolysis of the  $4\alpha,5\alpha$ -stereoisomeric epoxyketone in the same benzene-stannane system which furnished again both hydroxyketones, (XXVII) and (XXXIV), in an approximately reversed ratio<sup>†</sup>.

The irradiation experiments using stannane were also extended to the

<sup>†</sup> For similar epimerizations of *sec*- and *tert*-alkoxyradicals cf. reference 15.

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unsaturated epoxyketone (XXXV) which photorearranges to the  $\beta$ -diketone (XXXVI) in neat dioxane. Despite the analogous structural changes in the rearrangements to  $\beta$ -diketones of the saturated (XXIII) and the unsaturated epoxyketone (XXXV), the two respective primary photoprocesses differ distinctly. Contrary to the saturated compound, the conjugated epoxyketone is photostable when the long-wavelength transition ( $\lambda_{\max}$  333  $m\mu$ ,  $\epsilon$  64) is selectively excited. Rearrangement of (XXXV) occurs only when the conjugated ketone is promoted to the second excited singlet by irradiation in the second absorption band ( $\lambda_{\max}$  232  $m\mu$ ,  $\epsilon$  9000) with 253.7  $m\mu$ -light<sup>6</sup>. This is consequently another of the very few cases of conjugated carbonyl systems known at this writing<sup>16</sup> where a photoreaction takes place only from a higher energy excited state, competing successfully with internal conversion to the energetically lowest excited configuration. It is noted that, in addition to the C<sub>α</sub>-O fission (XXXV  $\rightarrow$  XXXIX) as proposed also for the rearrangement of the saturated epoxyketone (XXIII), another primary reaction mode is formally available to (XXXV): cleavage of the 5,10-bond to (XL) which could rearrange subsequently to (XLI) as the precursor of the final product (XXXVI).



Tri-*n*-butylstannane (0.74 M) proved to be sufficiently reactive to interact with 0.06 M unsaturated epoxyketone (XXXV) in dioxane solution upon irradiation with wavelengths  $>310\text{ m}\mu$ . The resulting major products were identified as (XXIII), (XXXVII), and (XXXVIII). In view of the photostability of (XXXV) in the absence of stannane but under otherwise identical irradiation conditions, the formation of these compounds is most likely due to photolytic reduction analogous to formulation (XXIII)  $\rightarrow$  (XXX). All three products can be derived from the resulting ketyl epoxide intermediate by appropriate secondary bond dissociations and/or addition of another hydrogen. It follows that the ability of (XXXV) to abstract hydrogen from the solvent or another solute is small relative to other conjugated ketones as, e.g., (III) which is already reduced by dioxane<sup>17</sup>. When in a second, similarly composed run the incident light was changed to wavelength 253.5 m $\mu$ , a qualitatively identical product pattern as above was obtained. Here again, part of the conversion to products, (XXIII), (XXXVII), and (XXXVIII), may be attributed to photolytic hydrogen abstraction presumably by molecules which have been deactivated previously to the lowest lying triplet state. However, it would seem plausible if the primary process of the epoxyketone rearrangement ( $\rightarrow$  XXXIX or XL) is not quenched by bimolecular reduction, with the former competing favourably with photophysical deactivation modes of the higher excited state. One or more of the products, probably (XXXVII) and/or (XXXVIII), would then be expected to result at least in part from hydrogen addition to the primary rearrangement intermediate.

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