

RECENT RESULTS ON SOME PHOTOCHEMICAL REARRANGEMENTS

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ABSTRACT

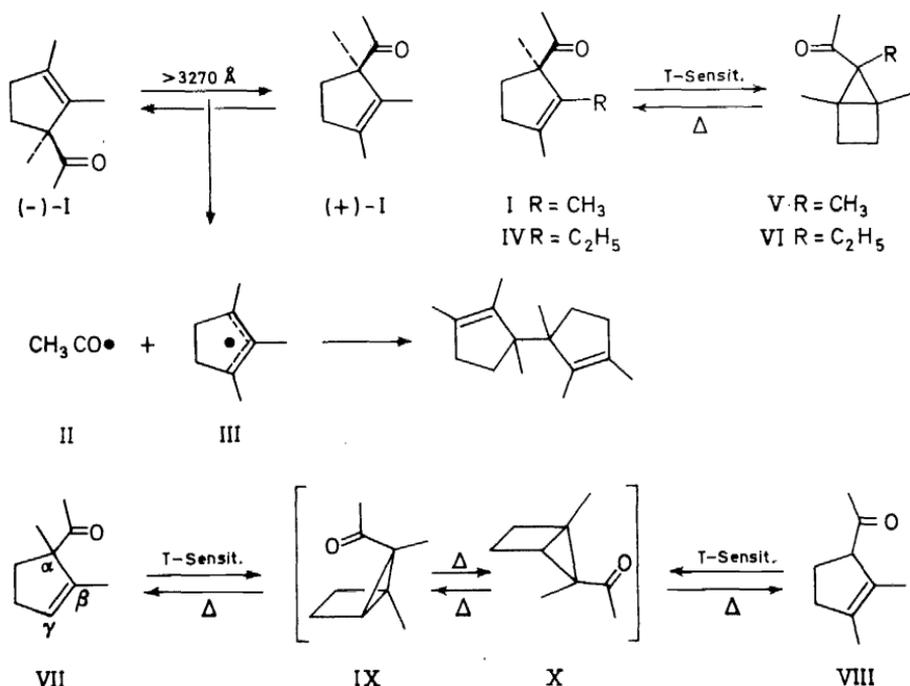
Reactions of α,γ -unsaturated ketones, 4-dimethoxymethyl cyclohex-2-enones, and dicyclopentadienones are reported: (1) the predominant photorearrangements of cyclopent-2-enyl methyl ketones are multiplicity-specific 1,3-acetyl shift in the singlet excited state and 1,2-acetyl shift and cyclization in the triplet. The analogous phenyl ketones undergo cleavage to triplet benzoyl/cyclopentenyl radical pairs which are shown to both dissociate into free radicals and recombine and disproportionate within the triplet 'cage'. (2) The dimethoxymethyl cyclohexenones undergo specifically $\pi \rightarrow \pi^*$ induced transformations: a 1,3-migration of the dimethoxymethyl substituent, and an abstraction of methoxyl hydrogen by the carbonyl oxygen which requires a distorted non-planar geometry of the enone excited state. (3) Thermal and photochemical interconversions of three isomeric dicyclopentadienones are discussed which involve formal suprafacial 1,3- and 3,3-rearrangements.

PHOTOCHEMISTRY OF β,γ -UNSATURATED KETONES

On direct photoexcitation aliphatic β,γ -unsaturated ketones preferentially undergo α -cleavage, whereas *cyclic* analogues have been observed to isomerize in formal 1,3-sigmatropic shifts of the acyl group as an alternative transformation¹. In our own work we directed investigations in this field to compounds with aliphatic acyl groups attached to cyclic olefins, and to the multiplicity requirements of the photorearrangement(s) of such compounds. A first report² concerned the findings that (1) singlet-triplet intersystem crossing in (I) is negligible, (2) reaction modes of the excited singlet state are, *inter alia*, 1,3-acetyl shift [(+) - (I) \rightleftharpoons (-) - (I)] and α -cleavage [(I) \rightarrow (II) + (III)], and (3) the triplet reaction almost exclusively is rearrangement to (V)[†]. The photoracemization of (I) in pentane accounts for over 32 per cent of the detectable singlet reaction, and it was shown to be entirely due to intramolecular acetyl migration. The acetone-sensitized rearrangement of (I) to (V)

[†] Specific dependence of the two rearrangement paths on multiplicity has since been observed with several β,γ -unsaturated ketones^{3,4}, and a possible explanation of the divergent behaviour of the singlet and triplet states based on spin distribution has been given⁵.

KURT SCHAFFNER



proved thermally reversible. Using the homologous compounds (IV) and (VI) both the photochemical triplet and the thermal reaction have now been found to involve 1,2-acetyl shifts⁶. Concerted photochemical $[\sigma^2 + \pi^2]$ and thermal $[\sigma^2 + \sigma^2]$ cycloadditions of the cyclopentenyl and the bicyclo[2.1.0]pentane system, respectively, are thus excluded, and the rearrangement (I) \rightarrow (V) corresponds to an 'oxa-di- π -methane' type process as encountered also in the triplet reactions of homocyclic and aliphatic β, γ -unsaturated ketones^{3, 4, 7}. Sensitization of the isomeric compounds (VII) and (VIII) furnished, in each case, an initial $\geq 7:1$ mixture of the *endo/exo*-isomeric products (IX) and (X)[†] which are not interconverted under the reaction conditions (acetophenone or acetone + 2537 Å)⁸. Possible mechanisms which allow for this stereo-selectivity of the triplet rearrangement are, e.g., the competitive occurrence of doubly antarafacial and suprafacial $[\sigma(\text{C}_{\text{CO}}-\text{C}_\alpha) + \pi^2]$ cycloadditions or, in view of the triplet nature perhaps more likely, $\text{C}_{\text{CO}}-\text{C}_\beta$ bridging followed by $\text{C}_{\text{CO}}-\text{C}_\alpha$ cleavage and cyclization between C_α and C_γ (with preferential utilization of the back lobe of the $\text{C}_{\text{CO}}-\text{C}_\alpha$ bond at C_α)[‡].

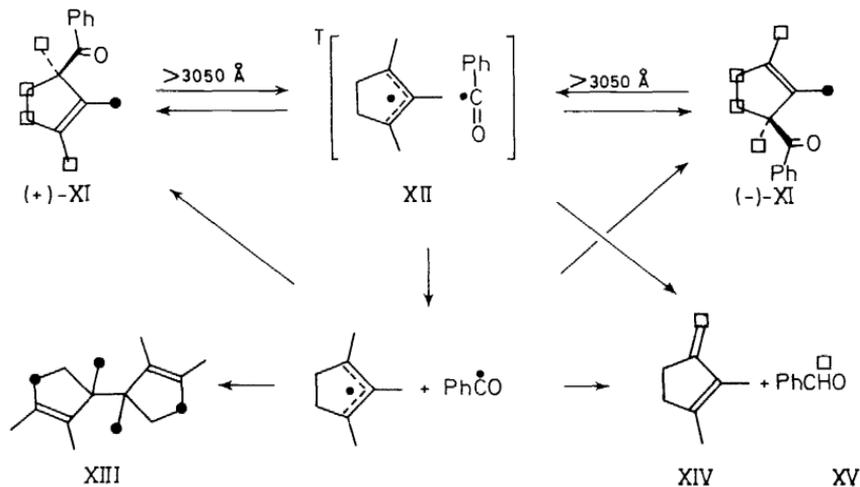
The optically active phenyl ketone (XI) photoracemized as well⁸. The formation of other products, *inter alia* some cyclopentenyl dimer (XIII) and substantial amounts of benzaldehyde (XV), was clearly more important

[†] The configurational assignment to products (IX) and (X) is based on the preparation of (X) from the corresponding *exo*-carboxylic acid which has been analysed by x-ray diffraction (private communication by Dr D. M. Hawley, University of Glasgow).

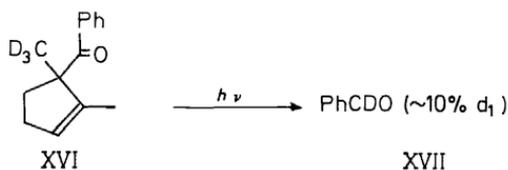
[‡] The thermal rearrangements (V) \rightarrow (I) and (IX)/(X) \rightarrow (VII)/(VIII) apparently follow the same route in reverse order. They are accompanied by *endo/exo* isomerization, presumably via a common cyclopentane 1,3-diradical^{8, 9}.

RECENT RESULTS ON SOME PHOTOCHEMICAL REARRANGEMENTS

than similar fragmentation processes of (I). The photolysis of a mixture composed of appropriately labelled derivatives of (XI) showed that, contrary to the case of methyl ketone (I), the photoracemization of the phenyl ketone (XI) is at least partially due to random recombination of free benzoyl and allylic cyclopentenyl radicals. This was confirmed in photolytic CIDNP (chemically induced nuclear polarization) studies conducted by Professor H. Fischer and B. Blank at the University of Zürich. The photolysis of (XI) induced strongly polarized resonances in compounds (XI), (XIII) and (XV). Furthermore, an absorption appearing at δ 4.6 was tentatively attributed to the vinyl protons of diene (XIV), a likely product resulting from the benzoyl/cyclopentenyl radical disproportionation affording benzaldehyde (XV). The formation of deuteriobenzaldehyde (XVII) in the photolysis of the deuterium-



CIDNP: \square Absorption
 \bullet Emission



labelled ketone (XVI) and the absence of the δ 4.6 absorption signal in a CIDNP experiment with (XVI) support this assignment. In additional CIDNP runs (XI) was irradiated in the presence of tri-*n*-butyl-stannane. While the polarization pattern and decay rate of the signals of (XI), (XIV) and (XV) were not affected, the polarization intensity decreased as a function of the stannane concentration until constant values were reached at $\geq 0.1\text{M}$ stannane. The CIDNP absorption and emission pattern of compounds (XI) and (XIII)–(XV) are consonant with product formation in free radical encounters and/or triplet pair (XII) reactions. The *partial* scavenging by stannane provides evidence that both routes contribute to the photochemical reaction of (XI).

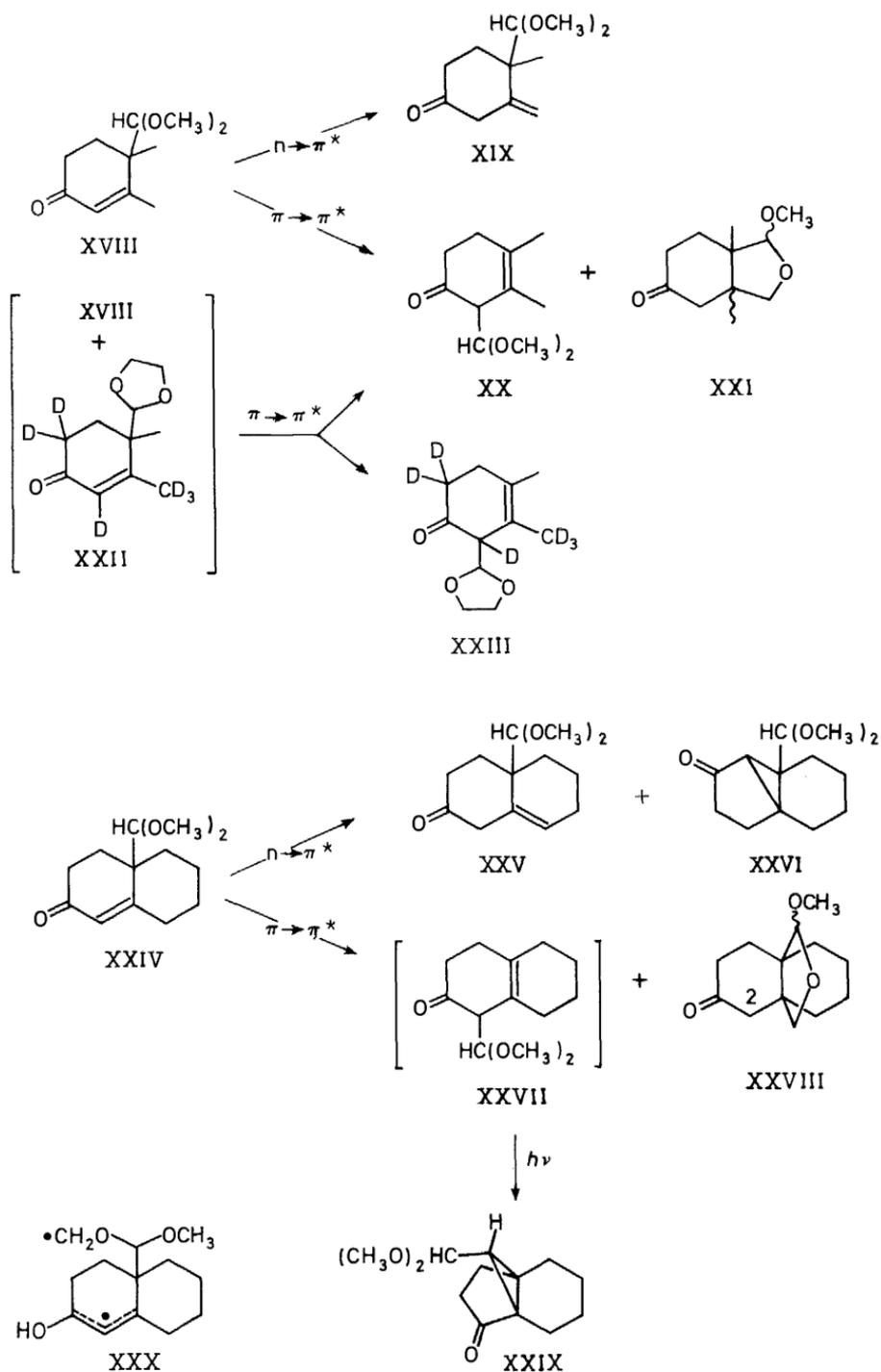
SPECIFICALLY $\pi \rightarrow \pi^*$ INDUCED REACTIONS OF
 α,β -UNSATURATED γ -DIMETHOXYMETHYL
KETONES

The α,β -unsaturated ketones (XVIII) and (XXIV) on $n \rightarrow \pi^*$ excitation at $\geq 3130 \text{ \AA}$ showed the expected triplet reactions¹⁰: double bond migration to the β,γ -unsaturated isomers (XIX) and (XXV)—due to intermolecular γ -hydrogen abstraction by carbonyl oxygen—as the predominant reactions in iso-octane solution, and relatively inefficient rearrangement of (XXIV) in *t*-butyl alcohol to the bicyclo[3.1.0]hexanone isomer (XXVI)^{11,12}. When compounds (XVIII) and (XXIV) were selectively excited in their $\pi \rightarrow \pi^*$ bands with wavelength 2537 \AA new reactions were observed which efficiently competed with the processes from the low-lying triplet state. Fragmentation of (XVIII) to a mixture of double bond-isomeric 3,4-dimethyl cyclohexenones and isomerization of (XVIII) and (XXIV) to (XX)/(XXI) and (XXVII)/(XXVIII), respectively, were now the major reaction paths. The β,γ -unsaturated ketone (XXVII) was photochemically quite labile and isomerized, presumably on sensitization by triplet excited enone (XXIV), to the cyclopropyl ketone (XXIX).

The transformations (XVIII) \rightarrow (XX) and (XXIV) \rightarrow (XXVII) are photochemical 1,3-sigmatropic shifts involving an sp^3 hybridized migrating carbon and novel in organic photochemistry[†]. Evidence for the intramolecular nature and hence concertedness was obtained in the photolysis of a mixture of (XVIII) and (XXII). The resulting 1,3-rearranged acetals (XX) and (XXIII) had retained the isotropic composition of the respective starting compounds and thus confirmed that no intermolecular exchange of the acetal substituents had occurred.

Two experiments proved particularly informative concerning the mechanism of formation of the hemicyclic acetals (XXI) and (XXVIII). The cyclization (XXIV) \rightarrow (XXVIII) was subject to a kinetic hydrogen/deuterium isotope effect of 2.7 as measured in a competitive experiment with a mixture of (XXIV) and its di-trideuteriomethoxy analogue (XXIV- d_6) in iso-octane solution. The isotropic composition of the starting ketone was fully retained in the resulting product (XXVIII- d_6). Furthermore, when (XXIV- d_6) was irradiated in *t*-butyl alcohol 34 per cent of the deuterium atom which was transferred to C-2 during the course of cyclization to (XXVIII- d_6), was exchanged for proton. These findings constitute evidence that the primary photochemical reaction is an intramolecular abstraction of methoxyl hydrogen by the carbonyl oxygen leading to the diradical intermediate (XXX). It is seen that the hydrogen transfer (XXIV) \rightarrow (XXX) for steric reasons becomes possible only when the enone excited state adopts a strongly non-planar conformation by an out-of-plane twist of the double bond. It is of interest to note that the equilibrium geometry of the lowest-lying π, π^* triplet state of similar enones qualitatively corresponds to this conformational condition¹⁵, but that the excited state for the specifically $\pi \rightarrow \pi^*$ induced conversions of (XVIII) and (XXIV) is evidently not accessible by intersystem crossing from the n, π^* singlet. A definitive assignment to the reactive excited state(s) responsible for the 1,3-

[†] Zimmermann¹³ recently reported a singlet process involving a concerted antarafacial vinylcyclopropane rearrangement. A formal example of a 1,3-sigmatropic shift of a γ -methylene group in an α,β -unsaturated ketone has been established to be non-concerted¹⁴.

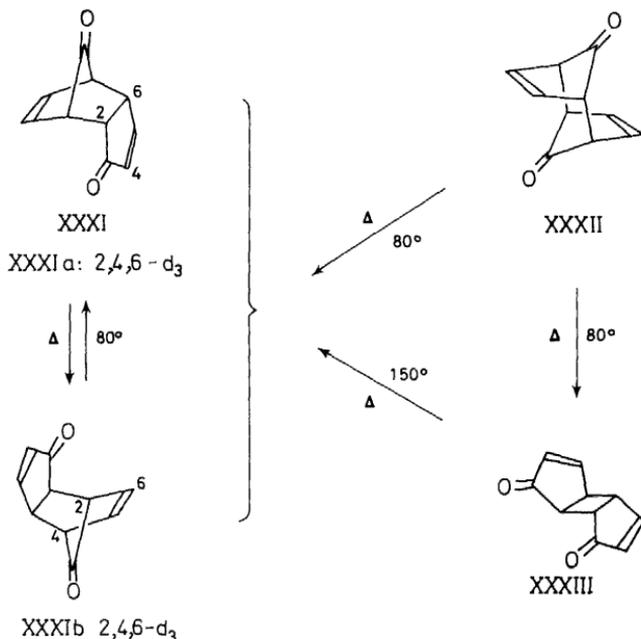


sigmatropic migration of the dimethoxymethyl substituent and for the intramolecular hydrogen abstraction, will have to discriminate between upper excited states (possibly including higher vibrational levels) in the π , π^* singlet or a triplet manifold†.

THERMAL AND PHOTOCHEMICAL INTERCONVERSIONS OF ISOMERIC DICYCLOPENTADIENONES

We have previously reported¹⁸ that irradiation of (XXXI) resulted in intramolecular 2 + 2 cycloaddition to the cage diketone (XXXIV) and in rearrangement to (XXXII), and on triplet sensitization with acetophenone the formation of (XXXIV) was observed. Furthermore, (XXXI) thermally decarbonylated above 100° to *cis*-8,9-dihydroindenone. In a recent re-investigation these findings could be extended¹⁹.

Dicyclopentadienone (XXXIa) which was selectively deuteriated at C-2, -4 and -6, at 80° in chloroform or hexachlorobutadiene underwent degenerate isomerization [\rightleftharpoons (XXXIb)]. Compound (XXXII) at 80° afforded about two parts (XXXI) and one part (XXXIII). At 150° (XXXIII) yielded quantitatively (XXXI).

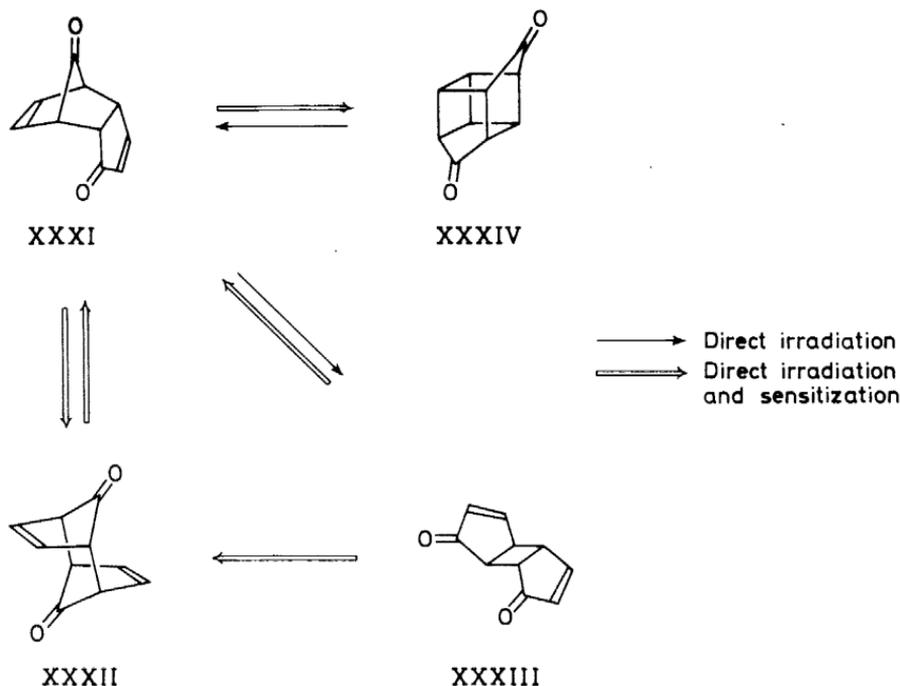


Excitation of (XXXI) with wavelengths $> 3400 \text{ \AA}$ or by sensitization with carbazole [both conditions under which (XXXIV) and (XXXII) remained unchanged] afforded 94 per cent (XXXIV) and six per cent (XXXII) (in benzene and acetonitrile). The product ratio also did not change on partial quenching

† A case of bimolecular hydrogen abstraction from an upper excited state has been reported by Ullman¹⁶. For other examples of specifically $\pi \rightarrow \pi^*$ induced enone reactions see reference 17.

with naphthalene, and a straight Stern–Volmer plot was obtained with 0.02–0.10M quencher. Both reactions, obviously resulting from different mechanistic paths, therefore occur from the same triplet excited state of (XXXI), irrespective of the mode of excitation.

The photoreactions $(XXXIV) \leftarrow (XXXI) \rightarrow (XXXII)$ were reversible. Ring opening of (XXXIV) [$\rightarrow (XXXI)$] was achieved by irradiation at $> 3050 \text{ \AA}$. The reactive state of (XXXIV) proved not amenable to diffusion-controlled triplet quenching by 3M 1,3-pentadiene, and attempted sensitization with acetophenone was unsuccessful. Compound (XXXI) was also regenerated from (XXXII) at 2537 \AA -radiation and on triplet sensitization with acetophenone. A more exhaustive analysis of the multiplicity of the reactions of (XXXIV) and (XXXII) is not available at present.



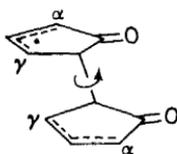
Irradiation of (XXXIII) at $> 3400 \text{ \AA}$ and sensitization with carbazole in acetonitrile gave 58 per cent (XXXI) and 42 per cent (XXXII). The difference between the product ratios from (XXXI) [(XXXIV)/(XXXII)] and (XXXIII) [(XXXI)/(XXXII)] is clearly too large to allow for the secondary transformation $(XXXI) \rightarrow (XXXII)$ in the latter photolyses as the only route to (XXXII), and thus establishes the additional direct conversion $(XXXIII) \rightarrow (XXXII)$. Attempted triplet quenching of $(XXXIII) \rightarrow (XXXI) + (XXXII)$ with 1M naphthalene and 3M 1,3-cyclohexadiene was not successful. The invariance of the product ratios (XXXI)/(XXXII) formed on singlet excitation and triplet sensitization is therefore only indicative for triplet reaction in the former case if either or both products (XXXI) and (XXXII) do not derive from (XXXIII) via a common state intermediate such as diradical (XXXV).

Owing to the considerably greater rate of conversion of (XXXIII) relative

to (XXXI) and (XXXII) ($\Phi_{(XXXIII)}/10 \sim \Phi_{(XXXI)} > \Phi_{(XXXII)}$), together with the greater absorbance of (XXXIII) in the entire ultra-violet region, compound (XXXIII) proved particularly elusive as a photoproduct. Its formation from (XXXI) could only be demonstrated in a photolysis of a mixture of (XXXIa) and non-labelled (XXXIII) at $> 3400 \text{ \AA}$. When the irradiation was stopped before (XXXIII) was fully consumed, the compound on recovery exhibited about two per cent of a deuterium label ($d_1 - d_3$) which corresponded in pattern to that of (XXXIa). It is possible, furthermore, that the photochemical degenerate isomerization of (XXXI) [cf. (XXXIa) \rightleftharpoons (XXXIb)] and the transformations (XXXI) \rightarrow (XXXIII) (sensitized) and (XXXII) \rightarrow (XXXIII) (direct and sensitized irradiations) are in fact also operating but have escaped detection.

Finally, the trideuteriated compound (XXXIa) was recycled thermally and photochemically via the deuterioanalogues of (XXXII) and (XXXIII). In all the transformations involved the original isotopic composition was fully retained in the products, demonstrating thus the intramolecular nature of the isomerizations. In particular, these results eliminate the *a priori* possibility of either thermal or photolytic fragmentation of (XXXII) and (XXXIII) into two cyclopentadienones followed by random thermal Diels-Alder dimerization to (XXXI).

The thermal isomerization (XXXIa) \rightleftharpoons (XXXIb)²⁰ and the photochemical transformations (XXXI) \rightleftharpoons (XXXII) and (XXXI) \rightleftharpoons (XXXIII) only are formal



XXXV

examples of allowed²¹ 3,3- (Cope rearrangement) and 1,3-suprafacial sigmatropic rearrangements, respectively. We note, however, that the photochemical isomerization of (XXXIII) follows the non-concerted path to (XXXII) about as efficiently as the formally allowed concerted rearrangement to (XXXI) [(XXXI):(XXXII) $\sim 35:65$ in benzene, $\sim 58:42$ in acetonitrile]. Non-concerted interconversions of compounds (XXXI), (XXXII) and (XXXIII) involve cleavage of a σ bond which is properly aligned in each case with allylic π -systems at both termini to facilitate this process, followed by internal reorganization of the diradical intermediate (XXXV) [$\alpha-\alpha$ bonding \rightarrow (XXXII), $\alpha-\gamma$ (XXXI), $\gamma-\gamma \rightarrow$ (XXXIII)]. The question remains—in view of the probable low activation energy required for the cleavage process—whether the concerted paths are in fact followed, the possibility existing that all thermal and photochemical rearrangements proceed along the two-step mechanism via the common intermediate (XXXV).

ACKNOWLEDGEMENTS

Important complementary contributions to the work of my collaborators Dr J. Gauthier, Mr J. Gloor, Mr H.-U. Gonzenbach, Dr U. Klinsmann.

and Mr M. Zink were provided by colleaguial efforts on the part of Professor Margaret J. Jorgenson, Boston University (deceased in March 1970; β,γ -unsaturated ketones and acetyl bicyclopentanes), Professor O. Jeger, ETH Zürich (γ -dimethoxymethyl enones), Professor H. Fischer and Mr B. Blank, University of Zürich (CIDNP experiments), and Professor B. Fuchs and Mr M. Pasternak, Tel-Aviv University (dicyclopentadienones). Financial support by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, Ciba-Geigy AG., Basel, Firmenich & Cie., Genève, and the National Research Council of Canada (for a scholarship to J.G.) are gratefully acknowledged.

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