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PHOTOCHEMICAL ALLYLIC AND DIALLYLIC REARRANGEMENTS

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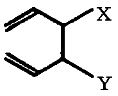
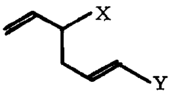
We have discovered a range of photochemical allylic rearrangements, which we would like to illustrate with some typical examples.*

In derivatives of diallyl (e.g. I); either one (II and III) or both allyl groups (IV) may shift. Irradiation of V[1] in cyclohexane with unfiltered light from a medium-pressure mercury arc caused rearrangement in good yield into the unconjugated isomer VI.



I



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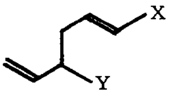

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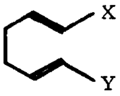
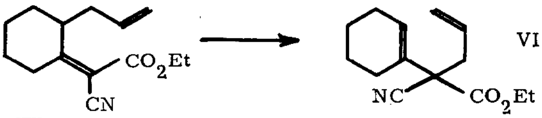


IV

V



VI

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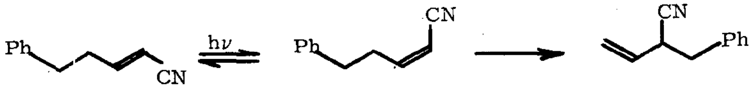
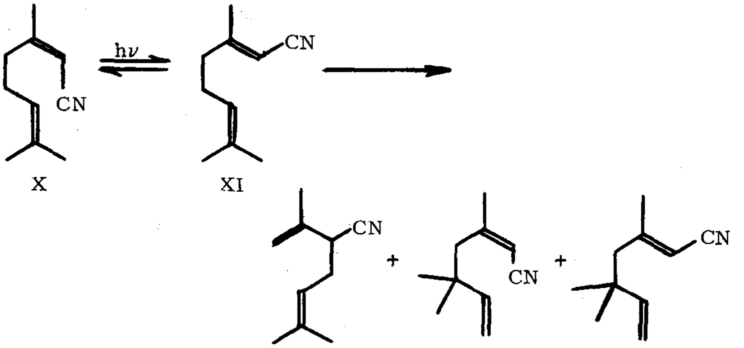
* All compounds gave satisfactory u.v., i.r. and p.m.r. spectra, and the structures were confirmed by unambiguous syntheses.

Under the same treatment the nitrile VII was converted into the *cis*-isomer VIII, and, more slowly, into the isomer IX in which the benzyl group had migrated (23% yield).



VII VIII IX

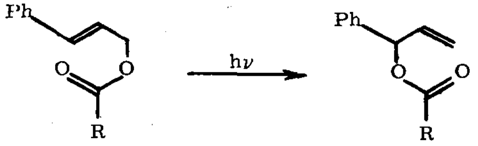
Geranonitrile[2] (X) rearranged into the isomers XII, XIII and XIV, but, as expected, the 6,7-dihydro-derivative was unchanged beyond *cis*-*trans* interconversion. Cinnamyl benzoate (XV; R = Ph) gave



X XI

XII XIII XIV

XV



XVI

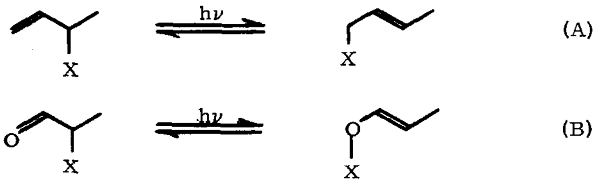
α-phenylallyl benzoate (XVI) in good yield apart from some polymerisation. The much slower rearrangement of cinnamyl acetate (XV; R = Me) to (XVI; R = Me) suggests that the benzoyl group plays a significant part in absorbing the light.

Thermally these reactions go in the reverse direction (e.g. VI ⟶ V; XVI ⟶ XV), so that in some cases the photochemical transformation may be useful in making the less stable, unconjugated isomer.

Although, naturally enough, cinnamyl acetate in cyclohexane was not affected by light filtered through Pyrex glass, in acetone rearrangement to (XVI; R = Me) proceeded. An even better yield (65%) of the benzoate was obtained with filtered light by using benzene containing cinchonine. These photo-sensitised reactions presumably take place through the triplet state of the styrene group[3] followed by cleavage into a pair of radicals that recombine, probably without diffusing apart. In the related photo-equilibrium[4] between 5α-acetoxy-Δ^3- and 3α-acetoxy-Δ^4-cholestan-7-one there is a ketone group within the molecule, which may have the same function. Whether the two oxygen atoms become equivalent during the migration will be settled only by their isotopic identification, but a concerted shift through a six-membered cyclic transition-state would be contrary to the symmetry of the orbitals in the first excited singlet state[5] (although the geometrically more difficult shift through a four-membered transition-state without inversion of the carboxy group would be allowed).

Several examples are now known[6] of the photochemical intramolecular rearrangement of bicyclic β,γ-unsaturated ketones, in which the acyl group migrates from one end to the other of the allyl group (scheme A; X = R.CO). The conversion of verbenone into chrysanthenone[7] provides a case where a quaternary carbon atom migrates in the same way (A; X = R.CMe_2). Recently several examples have been found in the oxygen system, where β-diketones and enol lactones or esters are interconverted[8] (scheme B; X = R.CO), and there is a special case here too (2,2,4,5-tetraphenyl-2,3-dihydrofuran ⟶ 1,1-diphenyl-2-benzoylcyclopropane[9]) involving the shift of a quaternary carbon atom (B; X = R.C.Ph_2).

Although nothing is yet known about the mechanisms of these reactions, it is possible that many of them too proceed through the triplet state and diradicals.



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