Photochemistry of the Extended Conjugated System 3-Oxoprop-1-enylcyclopropane of the Diterpene, Epoxylathyrol

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Summary The extended conjugated system of epoxylathyrol can be quantitatively isomerised by light to the *cis*, non-planar, enone (**7**), and thence to the fragmentation product (**3**), a furan.

WE have recently suggested[1] structure (**1**) for epoxylathyrol (euphorbiasteroid), a diterpene isolated from the caper spurge *Euphorbia lathyris L.*[2] This structure has been confirmed, and the *trans*-configuration of the double bond elucidated, by radio-crystallographic analysis.[3] In view of the continuing interest in the photochemistry of the cyclopropyl conjugated carbonyl chromophore in both cyclic[4] and acyclic[5] systems, the photochemical behaviour of (**1**) and its parent alcohol (**2**) has been investigated.

Irradiation† (Pyrex filter) of a solution of (**1**) in MeOH or C_6H_6 using a Philips HPK-125 mercury lamp, gave quantitatively in 1 h the furan (**3**). The n.m.r. spectrum of this photoproduct showed, in addition to signals attributable to the unchanged part of the molecule, new peaks characteristic of a 2,3-disubstituted furan and a trisubstituted double

† Irradiations were carried out under nitrogen, for 100 ml of a 0·1% solution.

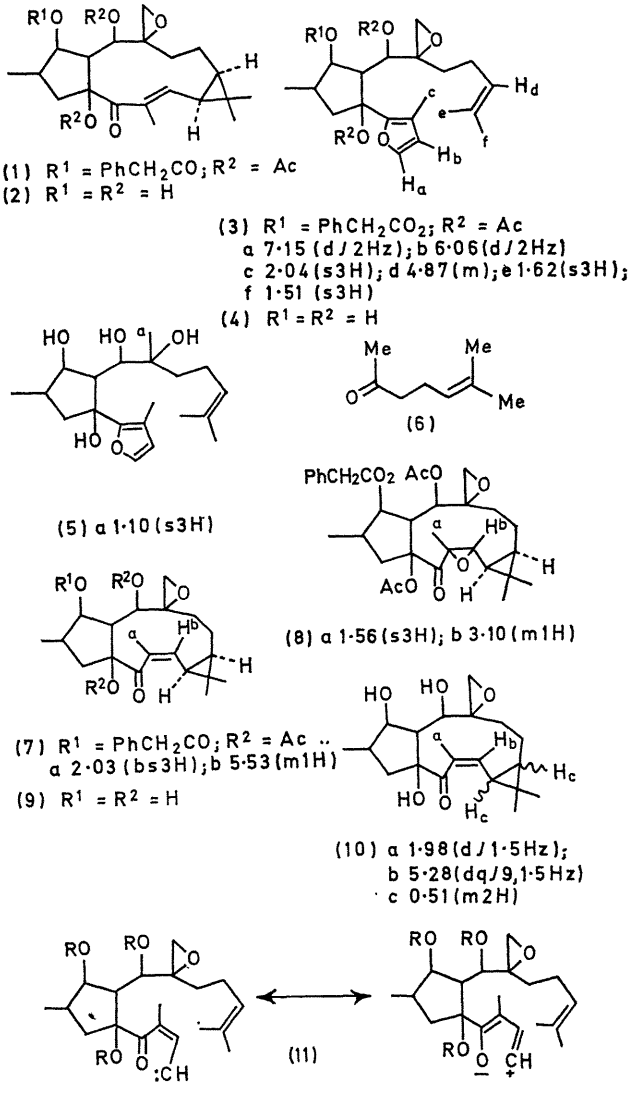
bond of the type $Me_2C{=}CH{-}$. An analogous substance (**4**) was obtained (but not quantitatively) from (**2**); its reduction with $LiAlH_4$ gave a tetraol (**5**), which on treatment with $NaIO_4$ provided methylheptenone (**6**) (identified by g.l.c. comparison with an authentic sample) as the only isolable fragment.

T.l.c. monitoring of the direct photolysis of (**1**) showed that formation of (**3**) was preceded by the formation of an intermediate product, the *cis*-enone (**7**). Isolation of this intermediate was facilitated by irradiating (**1**) in the presence of a photosensitiser (Me_2CO or PhCOMe), under conditions in which the sensitiser absorbed the major part of the incident radiation. In this way, a quantitative yield of (**7**) could be obtained from (**1**) in less than 10 min. The u.v. spectrum of (**7**) (λ_{max} 258 nm, ϵ = 1600) showed that the extensive conjugation of (**1**) (λ_{max} 273 nm, ϵ = 15,000)[1] had disappeared, while its i.r. spectrum showed no carbonyl absorption below 1705 cm^{-1}. These results are compatible with the presence of an enone group only if the C=O and C=C bonds are twisted out of conjugation.[6] The presence of the carbonyl group is confirmed by the circular dichroism of (**7**) which shows bands at 268, 330, and 355 nm ($\Delta\epsilon$ = + 1·80, + 0·04, and − 0·06 respectively). In agreement with the lack of conjugation, treatment of (**7**) with peroxy-acid gave the corresponding epoxide (**8**), m.p. 192–194°; c.d. bands at 320, 311, 301, and 293 nm ($\Delta\epsilon$ = + 1·04, 2·04, 2·23, and 1·81 respectively). The n.m.r. spectral characteristics of this compound support the assigned structure. Irradiation of (**7**) in the absence of sensitiser gave, as expected, the furan (**3**).

Direct irradiation of the parent alcohol (**2**) gave a transient substance (**9**) evidently analogous to (**7**), but this was converted not only into (**4**), but also into a minor photoproduct (15%), m.p. 160—162°, to which we assign structure (**10**). The spectra of this isomer exhibit most of the skeletal structural features of (**7**), (u.v.: λ_{max} 250 nm, ϵ = 1100; c.d.: bands at 317 and 250 nm, $\Delta\epsilon$ = + 0·47 and + 3·38 respectively), but in addition the protons of the cyclopropane ring give visible signals in the n.m.r. spectrum. This, together with the fact that no fragmentation is observed on both sensitised and direct irradiation, suggests that the cyclopropane ring is no longer in conjugation with the double bond, and that a stereoisomer has been produced. The data presently available do not allow definitive assignment of the geometrical arrangement at the cyclopropane ring.

This series of reactions can be interpreted as follows. The first step is the rapid *trans–cis*-isomerisation of the double bond, a reaction which is well known in the field of enone photochemistry,[7] and proceeds *via* a triplet mechanism. The resultant *cis*-enone (**7**) undergoes fragmentation because of overlap of the cyclopropane bonds with the adjacent π-system,[8] giving a resonance-stabilised carbene (**11**) of the correct geometry for cyclisation with the carbonyl group. This fragmentation takes place even in the presence of substantial concentrations of naphthalene, but only double-bond isomerisation is observed on triplet-sensitised irradiation (PhCOMe or Me_2CO). These results are consistent with previous observations[5,8] that the generation of carbenes from cyclopropanes proceeds by way of a singlet excited state. This reaction has precedent in the work of Jorgenson,[5] who reported the formation of α-alkoxyfurans as products of the photolysis of cyclopropyl acrylic esters. The efficiency of the reaction in our case is probably due to favourable ring constraints.

The ring-isomerised product (**10**) appears to derive from a triplet excited state, as it is the sole product of irradiation of (**2**) in the presence of sensitisers. The *cis–trans*-isomerisation of cyclopropane derivatives is a well documented



Epoxylathryrol and its photo-derivatives. Chemical shifts are given as δ-values.

photochemical process.[5,9] It is noteworthy that this reaction occurs only with the parent alcohol (**2**), and is not observed even after sensitised irradiation of (**7**) for several hours. This could be explained by the existence of conformational effects in (**7**) which preclude any rotation of the intermediate biradical which would lead to isomerisation.

The quantitative nature of the fragmentation reaction, which contrasts with the apparent lack of reactivity of cyclopropyl conjugated ketones in the acyclic series,[5] provides the first step of a potential degradation pathway for epoxylathyrol, as a preliminary to a biosynthetic study.

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