Stereochemistry of Oxacarbene Formation in the Photolysis of Oxacyclopentan-3-ones

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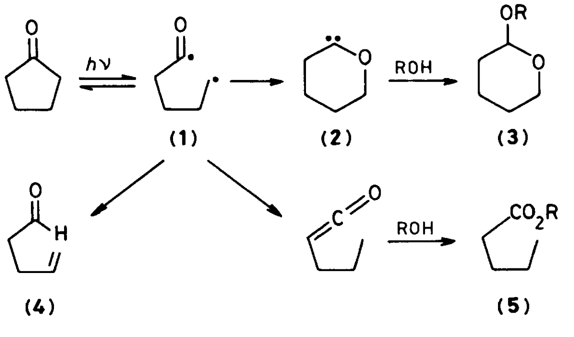
Photolysis of *cis*- and *trans*-3a,4,5,6,7,7a-hexahydro-3a-methylbenzofuran-3(2*H*)-one (**7**) in methanol gives similar mixtures of oxacarbene-derived acetals, showing that oxacarbene formation proceeds *via* an alkyl acyl biradical intermediate.

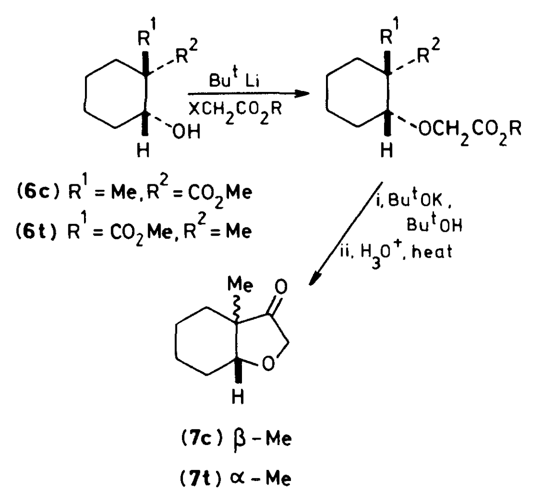
Previous investigations[1] have led to the proposal that the formation of cyclic acetals (**3**) on ultraviolet irradiation of five-membered cyclic ketones in alcoholic solution proceeds *via* cyclic oxacarbenes (**2**), which themselves arise from alkyl acyl biradicals (**1**) that are also the precursors of the more frequently observed photoproducts (**4**) and (**5**) (Scheme 1).



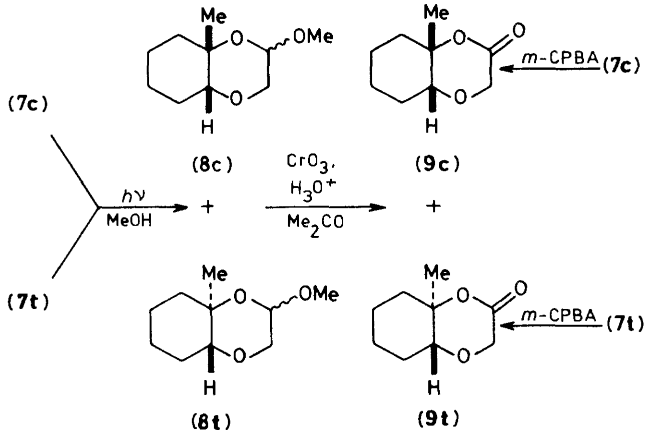
Scheme 1

Oxacarbene formation is normally unfavourable relative to the competing reactions of (**1**) and its occurrence depends on structural factors that facilitate it (*e.g.*, an α-cyclopropyl substituent or a β-annular oxygen atom) and/or inhibit the competing reactions.[2] By contrast, the formation of oxacarbene-derived acetals from cyclobutanones is a general reaction,[3] and the observation that it occurs stereospecifically[4,5] has led to the proposal that it involves a concerted reaction of the singlet excited state of the cyclobutanone and does not proceed *via* an alkyl acyl biradical.[5] We report now on the stereochemistry of the photochemical formation of oxacarbene-derived products from cyclopentanones, which has not been investigated previously.

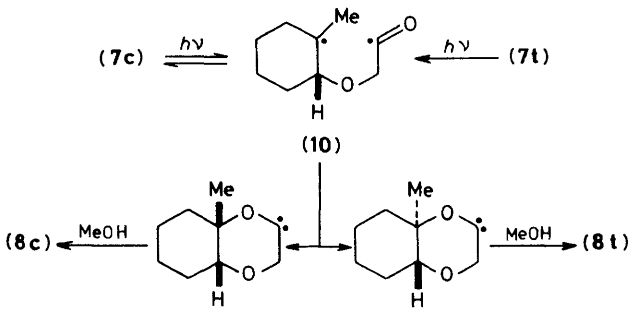
We chose the oxacyclopentan-3-ones (**7c**) and (**7t**), which we predicted would give oxacarbene-derived acetals as major products because of facilitation by the annular oxygen atom and inhibition of aldehyde and ketene formation. Compounds (**7c**) and (**7t**) were synthesized from the epimeric hydroxy esters (**6c**) and (**6t**)[6] by the route in Scheme 2 (all products obtained in the present investigation were racemic, but for



Scheme 2



Scheme 3. *m*-CPBA = *m*-chloroperbenzoic acid.



Scheme 4

convenience are represented as single enantiomers). In the case of (**6c**) the alkylation reaction was carried out with ethyl bromoacetate, while in that of (**6t**) it was necessary to use t-butyl iodoacetate because of predominant *O*-acylation by ethyl bromoacetate.

Irradiation of (**7c**) in methanol in the presence of sodium carbonate in quartz with an Hanovia 450 W medium-pressure mercury lamp led, after 4.5 hours, to the consumption of *ca.* 80% of the ketone and the formation of a *ca.* 12 : 1 mixture of the acetals (**8c**) and (**8t**) as the major products together with small amounts of aldehyde(s). The structures of the acetals, although not their anomeric composition, were established by their Jones oxidation to the corresponding lactones (**9c**) and (**9t**) and spectroscopic comparison of these with authentic samples obtained by Baeyer–Villiger oxidation of the ketones (**7c**) and (**7t**) (Scheme 3). Similar irradiation of (**7t**) led, after 9 hours, to the consumption of *ca.* 90% of the ketone and the formation of a *ca.* 10 : 1 mixture of (**8c**) and (**8t**) together with traces of aldehyde(s).

The formation of mixtures of (**8c**) and (**8t**) of very similar composition from each of (**7c**) and (**7t**) can be interpreted as resulting from reaction pathways that involve the common alkyl acyl biradical (**10**) (Scheme 4). Consideration must also be given to the possibility that (**7c**) and (**7t**) undergo photoequilibration *via* (**10**) prior to oxacarbene formation and that the latter then occurs in a concerted manner. Indeed, the ^{1}H n.m.r. spectrum of the photolysate from (**7t**) after 6 hours of irradiation showed the presence of both (**7t**) and (**7c**) in a ratio of *ca.* 3:2. However, the formation of (**7t**) from (**7c**) could not be detected at any stage of the photolysis of the latter, and thus prior photoequilibration of (**7c**) and (**7t**) is excluded.

The non-concerted photochemical formation of oxacarbenes from these oxacyclopentan-3-ones contrasts with the concerted pathway previously postulated in the case of cyclobutanones. This is in accord with the proposal that the primary photochemical reactions of cyclobutanones may differ from those of larger ring ketones,[5] and it lends strength to the earlier interpretation of the influence of structural features on the photoconversion of five-membered cyclic ketones into oxacarbenes.[2]

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