The Effect of Solvent on the Stereochemistry of Lumi-product Formation on Photolysis of a 2,5-Cyclohexadienone[1]

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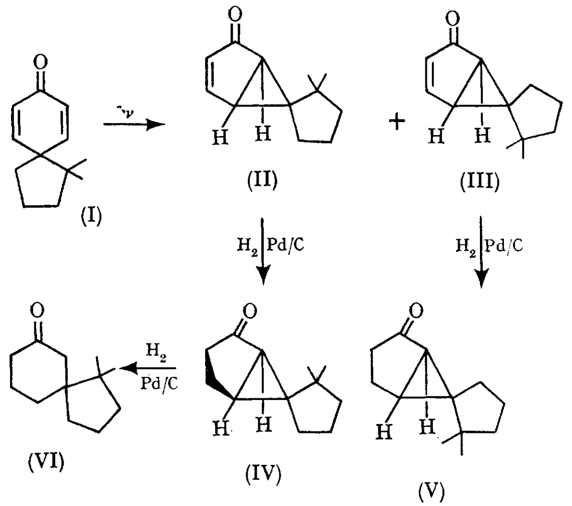
THE photochemistry of 4,4-disubstituted 2,5-cyclohexadienones has received considerable attention in recent years.[2] One of the principal reactions of these compounds is isomerization to bicyclo[3,1,0]hex-3-en-2-ones (lumi-products). While studying the photochemical behaviour of 2,2-dimethylspiro[4,5]-deca-6,9-dien-8-one (I), we observed an unusual solvent effect on the reaction leading to lumi-ketone.

Photolysis of (I) at 2537 Å affords the two epimeric lumi-ketones (II) and (III). Further photochemical transformations of (II) and (III) occur on extended irradiation and will be reported later. The yields of (II) and (III) are increased by irradiation at 2537 Å, as found in other analogous investigations.[2,3] Compounds (II) and (III) were obtained pure on separation by preparative gas chromatography and had the following spectroscopic data: i.r.: ν_{max} 1700 (carbonyl), 1630 (C=C), 1350 and 1375 cm.$^{-1}$ (*gem*-dimethyl); u.v.: λ_{max} 232 and 265 mμ; n.m.r. ($CDCl_3$), p.p.m.: δ1·92 and 2·45 (cyclopropane H), 5·70 and 7·35 (vinyl H), with coupling constants characteristic of the bicyclo[3,1,0]hex-3-en-2-one system;[3] mass spectra, *m/e*: 176 (molecular ion), 161, 120, 107, 96, 95, and 81.

The stereochemical assignments rest on the following observations:

(*a*) The methyl groups in compound (II) have n.m.r. resonances at δ 1·10 and 1·08, compared to 0·87 for those in (III). That the methyls in (II) are deshielded relative to those in (III) is reasonable, as molecular models reveal that the methyls in (II) are sufficiently close to the atoms of the cyclopentenone ring to experience a steric deshielding interaction.[5]



(*b*) Hydrogenation (Pd/C) of (II) and (III) affords the corresponding dihydro-compounds (IV) and (V). Compound (IV) shows methyl resonances at δ 1·00 and 1·20, and (V) at δ 0·82 and 0·87. The additional deshielding seen in (IV) is readily understandable on the basis of the proposed stereochemistry. Hydrogenation of the double bond leads to severe steric interactions between one of the methyl groups in (IV) and the cyclopentanone ring protons, thus increasing the magnetic deshielding.[5]

Compound (IV) readily undergoes further hydrogenation of the cyclopropane ring to afford compound (VI) (ν_{max} 1725 cm.$^{-1}$, *M* 180), while (V) does not react. This is consistent with the additional steric strain in (IV) and the problems associated with approach to the catalyst surface in (V).[6]

The effect of solvents on the photolysis of dienone (I) at 2537 Å was studied using a Hanau NK 6/20 lamp. The ratio (II) : (III) was determined by gas chromatographic analysis on Carbowax 20 M, and the results for 1.0 hr. irradiations are given in the Table. Irradiations for longer periods gave very similar, or in some cases slightly smaller, ratios due to somewhat faster consumption of (II) in further transformations. Experiments with pure samples of the epimers (II) and (III) showed that they were not interconverted photochemically under any of the conditions used in the study. In the protic solvents, methanol and t-butyl alcohol, there is a preference for (II), which is maintained in dioxan. The ratio is close to one in ether and benzene, while it reverses in favour of (III) in hexane and cyclohexane. Since the quantum yield for appearance of the lumiketones (II) and (III) in dioxan at 2537 Å is 0·6, no significant amount of reversal of the isomerization is possible, so that the ratio (II) : (III) reflects kinetic and not equilibrium control. Although solvent effects are known in a number of photochemical processes, there is no precedent for these observations. In the three reported examples where more than one stereoisomeric lumiketone was obtained from a dienone, no solvent studies were reported.[3,7]

TABLE

Ratio of (II) : (III) *on* 1·0 *hr. irradiation of* (I)

Solvent	(II) : (III)
Methanol	2·50
Bu^{t}OH	2·04
Dioxan	1·23
Ethyl ether	1·11
Benzene	1·09
Hexane	0·91
Cyclohexane	0·79

The solvent effect on the stereoselectivity can be understood on the basis of the Zimmerman–Schuster mechanism for the transformation of dienones to bicyclic lumiketones, in terms of preferential solvation of the diastereoisomeric intermediates leading to the two products.[2,8]

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