Two New Products from the Photoisomerization of Eucarvone

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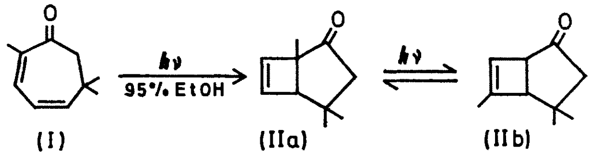
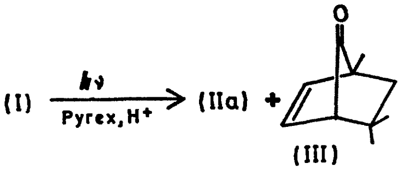
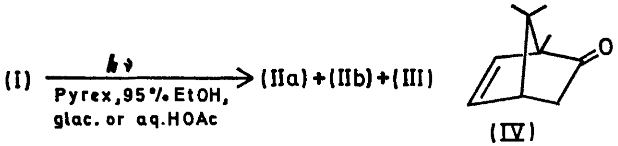
Summary Irradiation of eucarvone (I) adsorbed on silica gel or in trifluoroethanol gives, in addition to the two expected products (IIa and IIb), the bicyclo[4,1,0]enone (V), which subsequently undergoes [1,3]sigmatropic photorearrangement to dehydrocamphor (IV) and a cyclobutanone (VI).

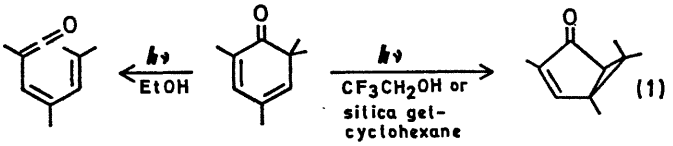
THE photosomerization of eucarvone (I), initially studied by Büchi and Burgess,[1] was the first example of a general photo-reaction, *i.e.* 1,3-acyl migration in $\beta\gamma$-unsaturated ketones [(IIa) $\rightleftharpoons$ (IIb)].[2] Later, Hurst and Whitham[3] obtained equal amounts of (IIa) and a third product (III) by irradiating (I) in acid:





Schuster, Nash, and Kantor[4] detected a fourth product, dehydrocamphor (IV). Though all four products were observed in all solvents and (IIa) always predominated, the relative ratios were solvent dependent. Ionic mechanisms have been proposed[1,3-5] for the direct formation of (IIa, (III), and (IV) from (I), although the possible need for intermediates has been recognized.[4]

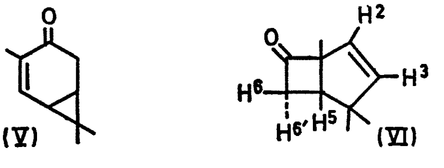




Recently we described[6] a dramatic solvent effect on the photoisomerization of 2,4-cyclohexadienones (Equation 1). Trifluorethanol or silica gel caused a large bathochromic shift of the π,π^* band of cyclohexa-2,4-dienones, halted the customary photoisomerization to ketenes (an n,π^* reaction), and gave instead bicyclo[3,1,0]hexenones.

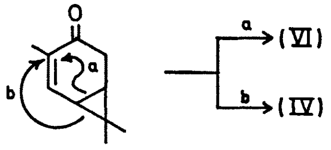
We have investigated the photochemistry of the cyclohepta-2,4-dienone eucarvone (I) adsorbed on silica gel and in trifluoroethanol solution. Compound (I) has a broad, intense λ_{max} (EtOH) at 303 nm (log ϵ 3·83)[7] which is shifted, without appreciable change in intensity, to 310 nm in $CF_3{\cdot}CH_2OH$ and to 318 nm in silica gel–cyclohexane. We observed that the photoisomerization of (I) is greatly accelerated in these strongly polar media, that two new products are formed, and that (IV) is derived from one of these, and probably not directly from (I).

Irradiation of (I)[8] adsorbed on silica gel† (Hanovia 450 w lamp, 6hr., in Pyrex) gave (g.l.p.c.) 11% of recovered (I), 43% (IIa), 17% (IIb), a trace of (III), 7% of (IV) and two previously unobserved products‡ assigned structures (V) (9%) and (VI) (13%). Under comparable conditions, irradiation of (I) in cyclohexane solution gave 11% of (IIa) and 89% recovered (I).



The structures of (V) and (VI) were deduced from their spectra: (V), n.m.r. one vinyl H (τ 3·35) and one allylic methyl (8·27) mutually coupled (J = 1·5 Hz), and two aliphatic methyl singlets (8·78, 9·15): i.r. and u.v. spectra virtually identical with those previously reported.[9]

Compound (VI) was clearly a cyclobutanone ($\nu_{C=O}$ 1770 cm^{-1}) with a methylene group adjacent to the carbonyl (the mass spectrum showed an intense peak at m/e 108; $P - 42$). A 100 MHz n.m.r. spectrum showed two vinyl protons (τ 4·47, 4·70, J = 5·5 Hz) and three doublets of doublets corresponding to H^6 (τ 6·92, J = 7·0, 18·0 Hz), $H^{6'}$ (τ 7·33, J = 8·0, 18·0 Hz), and H^5 (τ 7·92, J = 7·0, 8·0 Hz. The u.v. spectrum showed the expected[10] enhanced absorption for a $\beta\gamma$-unsaturated ketone with this geometry.§



In kinetic experiments, the percentage of (V) in the photolysis mixture rose to a maximum (20% in 3 hr.), then decreased. Direct irradiation of (V) on silica gel–cyclohexane through Pyrex converted it (6 hr.) into a mixture

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† U.v. examination of the solvent withdrawn from samples prepared as described showed that >99% of the dienone was adsorbed by the silica gel.

‡ Previously reported photoproducts were identified by their i.r. and n.m.r. spectra. Control experiments showed that eucarvone was recovered (>95%) even after 10 hr. reflux with silica gel–cyclohexane in the dark, that all the photoproducts [except (III), which was not tested] were stable toward silica gel–cyclohexane (12 hr., dark, room temperature) and that each compound was stable to the g.l.p.c. conditions.

§ Detailed arguments which conclusively eliminate the three isomers of (VI) in which either the C-1 methyl and C-5 hydrogen or the C-6 methylene and C-7 carbonyl positions are interchanged will be presented in the full account.

of (IV) (35%) and (VI) (65%). This reaction can be regarded formally as a 1,3-suprafacial shift.[11]

Compound (IIa) was converted photochemically into (IIb) and no other products, but much more slowly on silica gel–cyclohexane than in cyclohexane solution.

We conclude that irradiation of eucarvone on silica gel–cyclohexane takes two independent paths as shown in the Scheme:

$$\begin{tikzcd}
 & (IIa) \arrow[r, shift left, "h\nu"] & (IIb) \arrow[l, shift left] \\
(I) \arrow[ur, "h\nu"] \arrow[dr] & & \\
 & (V) \arrow[r, "h\nu"] & (IV)+(VI)
\end{tikzcd}$$

Similar results were obtained by irradiating (I) in CF_3CH_2-OH solution through Pyrex, but in cyclohexane solution (IV) and (V) were not observed even when the irradiation was carried out through quartz [though 1—3% of (VI) was observed under these conditions]. Only trace (< 1%) amounts of (III) were formed, except in acidic (HOAc, H_2SO_4) solvents.

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