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LASER PHOTOCHEMISTRY: THE INTRAMOLECULAR CYCLIZATION OF CARVONE TO CARVONECAMPHOR

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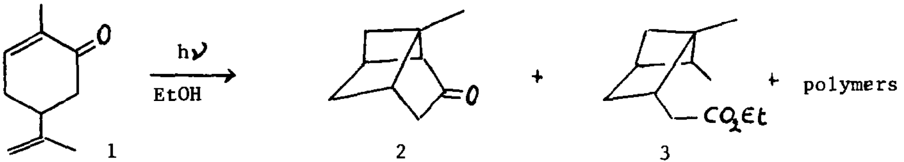
Abstract: Kr-ion laser irradiation of carvone (1) at 350.7 and 356.4 nm gave carvonecamphor (2) in a much higher yield (88%) than in conventional photochemistry, while (3) was a primary photo-by-product.

Photocycloadditions of α,β-unsaturated ketones to olefins have long excited the interest of natural product chemists in connection with the origin of terpenes in nature.[1] Since then, they have also gained general synthetic importance in the area of four-membered carbocyclics,[2] but the yields are often poor. Taking the representative example of the photocycloaddition of carvone (1) to carvonecamphor (2), it took fifty years from the early study, employing the sun as a light source,[1a] before firm structural proof for 2 was given.[1b] However, the problems remained of both the poor yield of cycloadduct (9%) and the excessive long irradiation times (6-12 months).[1b] A partial solution to such problems came from the use of either Hg-vapor lamps or, with better results, black light fluorescent lamps as light sources.[2] Thus, 2 was obtained, within some days, in a 40% yield as the best balance among further photolysis of 2 into 3 and disappearance of as much as 40% of the starting 1 to give polymers.



1 2 3

With the aim to change such an unfavourable but interesting situation we have undertaken an investigation of enone-olefin photochemistry, just beginning with the case of 1, by the use of a powerful continuous-wave Kr-ion laser (Spectra-Physics mod. 1-171). This choice met our primary aim of irradiating the enone at the long wave tail of its n-π^*absorption band [for 1: λ_{max} (EtOH) = 320 nm, $\varepsilon = 45$], out of the absorption of the cycloadduct [for 2: λ_{max} (EtOH)=296 nm, $\varepsilon = 40$]. Thus, using both the 350.7 and 356.4 nm emission lines jointly, under starting total absorption of the 1 W radiation power by the reaction mixture, we irradiated 2.5 ml of a 0.06 M ethanolic solution of (-) -carvone, which was made to flow continuously through a cylindrical quartz cell of 100 mm optical length and 10 mm^2 cross section under nitrogen. Within 1.5 h 1 was transformed into 2 (88%), 3 (8.2%) and polymers (3%), while only traces of unreacted 1 were detectable by glpc. It is also interesting that: *i* ethanolic solutions of 2 were stable under irradiation for long periods; *ii* the concentration of both 2 and 3 increased linearly with the irradiation time as long as total absorption conditions were satisfied; *iii* both naphthalene and 2,4-hexadiene depressed the photoproduction of both 2 and 3 from 1, naphthalene being most affective (linear Stern-Volmer plots indicate that a bimolecular process of quenching is operative in both cases).

Such a dramatic increase of the yield of the intact cycloadduct 2 is clearly due to the combined effects of having both entirely suppressed the photolysis of 2 into 3 and greatly diminished the formation of polymers, which were wasting processes during previous irradiations.[2] Suppression of the photolysis of 2 into 3, as proved by point *i* above, is due to selective irradiation of 1 out of the absorption regions of 2, as desired when selecting the light source. However, formation of 3 is a unavoidable process, to some extent, during ultraviolet irradiation of 1. This is because 3 is a primary photoproduct of the irradiation of 1, as shown by points *i* and *ii* above, which was never recognized before (the quantum yields for the formation of 2 and 3 were, respectively, $1x10^{-3}$ and $8x10^{-5}$).

As to the origin of 2 and 3, these is evidence (point *iii* above) that 2 and 3 arise from a common excited triplet 1^* when it is recalled that both naphthalene and 2,4-hexadiene are known as triplet quenchers for energy donors with E_T greater than 61 and 59 Kcal mol^{-1}, respectively.

Finally, light-intensity effects of the type recently discovered by Schuster and al.[4] can be ruled out in the case of carvone because the quantum yield for the transformation of 1 and 2 did not change on changing the laser power from 1 to 0.5 W.

From both these and previous results[5] we conclude with the suggestion that the use of UV lasers may prove to be useful in other cases where the photochemical analogue of the Kasha's rule[6] is not followed. If so, the availability of powerful *tunable* lasers in the near UV is much needed.

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