The Unexpected Photodecarbonylation of Bicyclo[3,2,1]oct-2-en-8-one in Solution

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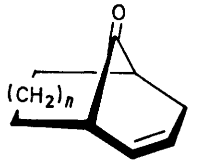
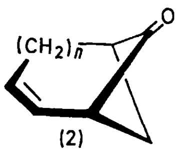
Summary Irradiation of bicyclo[3,2,1]oct-2-en-8-one in hydrocarbon solvents leads to photodecarbonylation as the preferred reaction pathway accompanied to a lesser extent by the previously reported photoisomerization to bicyclo[4,1,1]oct-2-en-8-one.

ERMAN AND KRETSCHMAR reported[1] that the photoisomerization of $\beta\gamma$-unsaturated bicyclic ketones of type (**1**) provided a useful synthetic route to the otherwise not readily accessible cyclobutanones of type (**2**) ($n > 1$).



(1)



(2)

(3)

We report that in the case of at least one of the representative examples of this study,† extensive decarbonylation is

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† The photochemical behaviour of the other examples is also being investigated.

the preferred reaction pathway rather than photoisomerization

Since bicyclo[4,1,1]oct-2-en-8-one (**2**, $n = 2$) was required as an intermediate in our studies on highly strained molecules its synthesis *via* the reported[1] photoisomerization of bicyclo[3,2,1]oct-2-en-8-one (**1**, $n = 2$) was attempted Major discrepancies in our quantitative results with those reported prompted us to monitor the progress of the reaction carefully

A pentane solution‡ of bicyclo[3 2,1]oct-2-en-8-one (**1**, $n = 2$) containing 4% of its dioxolane-derivative as internal standard was irradiated for 130 min with a 200W GE medium-pressure mercury lamp fitted with a Vycor filter ($\lambda > 210$ nm) Periodic g l p c analysis§ indicated that in addition to the formation of the desired isomeric ketone a major new component was formed which was eluted at a considerably shorter retention time than the two isomeric ketones Purification of this product by preparative g l p c afforded a volatile liquid fraction which was identified as 2-norcarene (**3**) from its spectral data ¶ The concentration relationship of the various components as a function of the exposure time is shown in the Figure After 90 min of irradiation, the isomeric ketone constituted only 10% of the reaction mixture, together with almost 35% of 2-norcarene (*ca* 45% yield)

The optimum exposure time for the maximum yield of the isomeric ketone (*ca* 22%) appears to be only 30—35 min It is also noteworthy that the concentration of 2-norcarene could be enhanced by irradiation at −60° but with almost no change in the maximum yield of the desired ketone Although photodecarbonylation could be suppressed by irradiating through a Pyrex filter at room temperature, the maximum yield of bicyclo[4,1,1]oct-2-en-8-one (**2**, $n = 2$) remained essentially the same

The mechanism of photodecarbonylation of ketones[3] and aldehydes[4] in solution is a topic of much present interest The report by Schaffner *et al*[4] represents an excellent mechanistic study on the solution photodecarbonylation of $\beta\gamma$-unsaturated aldehydes, but literature on the detailed mechanistic aspects of the analogous reaction of cyclic and polycyclic $\beta\gamma$-unsaturated ketones are almost non-existent[5] Both the ease of this liquid phase decarbonylation and its selectivity in giving (**3**) in preference to the apparently equally likely isomer, bicyclo[3,2,0]hept-2-ene, are remarkable

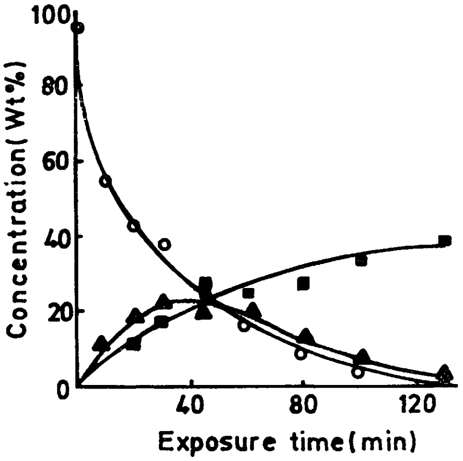

FIGURE *Concentration of major components as a function of time of irradiation*, ○—bicyclo[3,2,1]oct-2-en-8-one (**1**, n = 2), ▲—bicyclo[4,1,1]oct-2 en-8-one (2, n = 2), ●—2-norcarene (3).

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‡ While the results were similar when the original solvent, cyclohexane, was used, the separation of the hydrocarbon product is much more easily accomplished in the lower boiling solvent

§ A column of 6 ft × $\frac{1}{8}$ in 30% Carbowax 20 M on 60/80 Firebrick was used, column temperature was programmed from 40—100°

¶ We thank Prof Dr Georg Wittig, Institut fur Organische Chemie, Universitat Heidelberg for sending us the spectral data of 2-norcarene prepared according to an independent procedure[2]

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[4] E Baggiolini, H P Hamlow, and K Schaffner, *J Amer Chem Soc* , 1970, **92**, 4906

[5] Preliminary mechanistic details were given in a few reports on the relationship between structural features and photodecarbonylation of unsaturated ketones D I Schuster, F -T H Lee, A Padwa, and P G Gassman, *J Org Chem.*, 1965, **30**, 2262 J E Starr and R H Eastman, *ibid* , 1966, **31**, 1393 and references therein