

PHOTOCHEMISTRY OF ORGANIC HALIDES: SOME INTERESTING  
FEATURES OF THE PHOTOBHAVIOUR OF VINYL HALIDES AND  
VINYLIDINE DIHALIDES DERIVED FROM CAMPHENE

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**SUMMARY:** A study of the photochemistry of vinylidene dihalides 1 and 2 and vinylhalides 4 and 5 revealed some interesting differences in their photobehaviour. This study led to uncover an important constraint in the generation of vinyl cations from certain  $\alpha$ -unsubstituted vinyl halides such as 4.

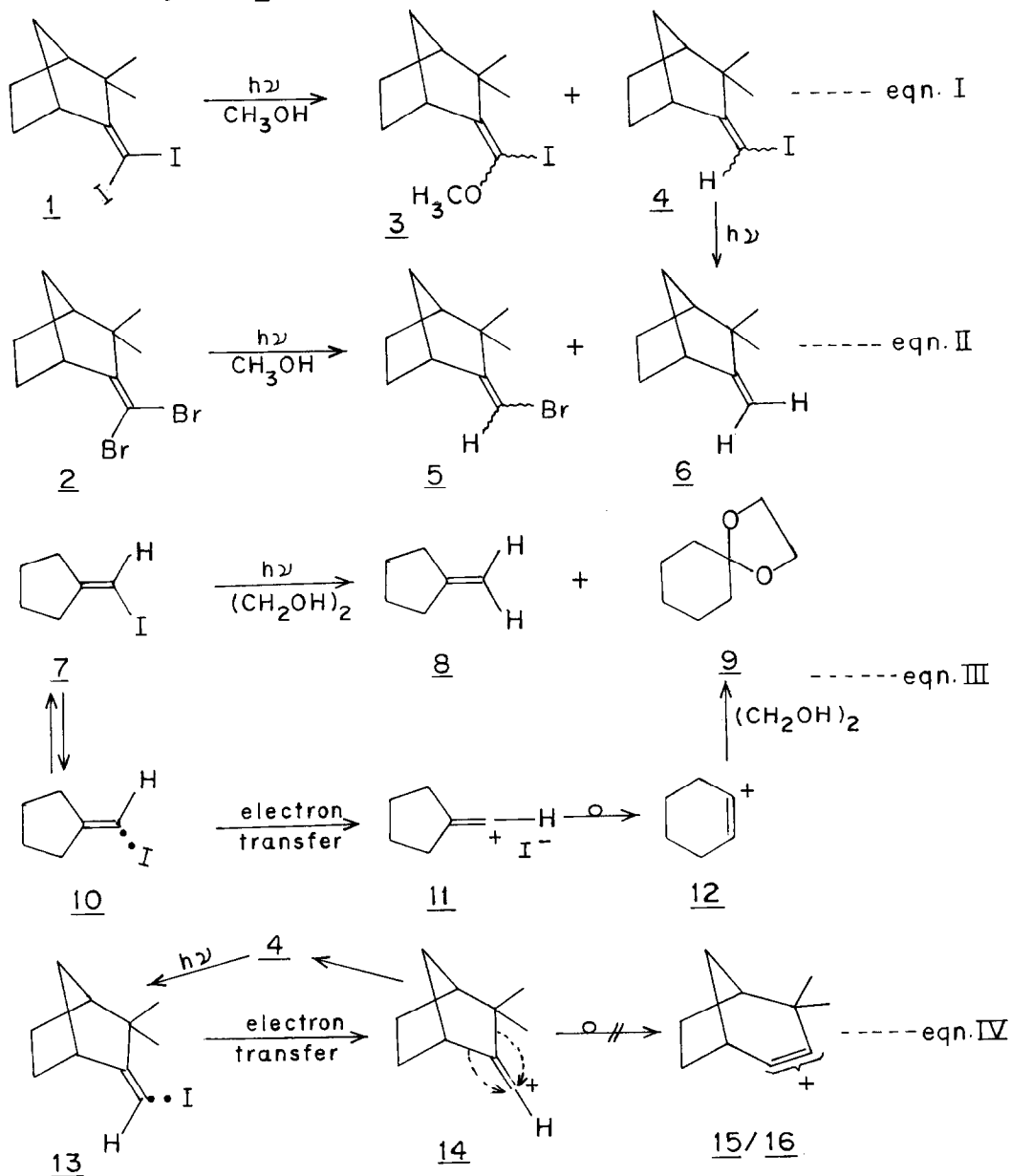
During the past few years, the photochemistry of organic halides has received fairly considerable attention<sup>1</sup>; however, a similar study of 1-halo and 1,1-dihaloethylenic chromophores has comparatively remained unexplored in spite of their presence in synthetic pyrethroids<sup>2</sup>, a highly potent class of insecticides. We have recently examined<sup>3</sup> the photobehaviour of a group of vinyl halides derived from camphene and demonstrated that in addition to polar medium, the presence of a stabilizing  $\alpha$ -substituent is the primary need to generate vinyl cations.

In this communication we wish to present the results of the photochemistry of a pair of vinylidene dihalides<sup>4</sup> 1 and 2 and compare their photobehaviour with those of the corresponding vinyl halides 4 and 5 under similar conditions. This study reveals the importance of ring strain in the photochemistry of exo-methylene  $\alpha$ -unsubstituted vinyl iodide 4 wherein an alteration in the typical ionic behaviour of the C-I bond in favour of a radical pathway is observed; a phenomenon probably first of its kind.

Irradiation of 1 in anhydrous methanol (0.8% soln. N<sub>2</sub>, 200-W high pressure Hanovia lamp, 9 hr) at room temperature<sup>5</sup> afforded principally two primary photoproducts<sup>6</sup> 3 and 4 (~1:1, glc, 88% yield, eqn-I). When irradiation was continued further, the disappearance of 4 with concomitant formation of 6 was observed. However, irradiation of 2 under similar conditions (16 hr) furnished exclusively the partial reduction product 5 (82% yield) with no indication (glc, pmr) of the appearance of any other product except 6 formed on prolonged irradiation (eqn-II).

It is interesting to note that when 1 and 2 were subjected to irradiation at low temperature (~ -10°C), 2 did not offer any ionic product even in trace quantities, while the diiodo compound 1 furnished essentially the ionic product 3 in a high yield (90%). Thus photolysis of 1,1-diiodoethylenes especially at low temperature can be considered to be a preparative method to obtain interesting class of compounds such as 3. However, it is significant to note that independent photolysis of halides 4 and 5 at ambient and even

at low temperature ( $\sim -20^\circ\text{C}$ ) failed to furnish any ionic product, instead afforded only the reduction product 6.



The significant features of the present results are as follows: The two dihalides 1 and 2 exhibit a highly contrasting photobehaviour; the former afforded both ionic 3 and radical products 4, whereas the latter furnished exclusively radical products. The only known example of analogous contrasting photobehaviour of vinylidene diiodides and dibromides is that of (dihalomethylene) cyclohexanes<sup>7</sup>. This difference

in behaviour has been ascribed to the intrinsic nature of C-I and C-Br bonds<sup>8</sup>.

The most intriguing observation is that the vinyl iodide 4 refused to give any ionic product, while the corresponding diiodide 1 under similar conditions furnished predominantly the stable nucleophilic trapping product 3, though in both the cases the photocleavage involves the common C-I bond.

In this regard, attention may be drawn to the recently reported<sup>7</sup> photobehaviour of iodomethylene cyclopentane 7 which on irradiation in ethylene glycol afforded the ionic product 9 with a ring enlargement along with the reduction product 8 (eqn-III). Similarly, only the ring-enlarged ionic product was obtained from iodomethylene cyclohexane also. These results have been rationalized by assuming the ready rearrangement of the initially formed unsubstituted vinyl cation 11 to  $\alpha$ -substituted endocyclic vinyl cation 12 which on encapture by the solvent furnishes 9. It appears that the rearrangement is a characteristic feature of  $\alpha$ -unsubstituted vinyl cations although the resulting endocyclic vinyl cation cannot assume the preferred linear geometry.

In view of the above results, the initially generated  $\alpha$ -unsubstituted vinyl cation 14 from 4 was very much expected to rearrange to  $\alpha$ -substituted vinyl cation 15 or 16 and furnish the products therefrom (eqn-IV). However, it is interesting to note that such products are conspicuously absent. This unexpected deviation in the photobehaviour of 4 may be attributed to the strain<sup>9</sup> involved in accommodating a bent vinyl cation in bicyclo(3.2.1)octane system. Since this pathway appears to be one of high energy, the ion pair 14 prefers to revert to the starting halide. Instead, the other low energy competitive pathway involving the radical pair 13 leading to reduction product 6 is followed.

Although C-I bond in general is known<sup>7</sup> to show a proclivity under photolytic conditions for the formation of ionic products, the present study shows that in the case of iodomethylenecycloalkanes there are certain constraints; the formation of ionic products appears to be controlled by the ability of the ring system to accommodate a bent vinyl cation<sup>10</sup>.

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#### REFERENCES AND NOTES

- 1 P.J. Kropp, Acc. Chem. Res., 17, 131 (1984) and references cited therein.
- 2 M. Elliot and N.F. Jones, Chem. Soc. Revs., 7, 473 (1978).
- 3 (a) H.R. Sonawane, B.S.Nanjundiah and S.I. Rajput, Ind. J. Chem., 23B, 331 (1984);  
(b) H.R. Sonawane, B.S.Nanjundiah and S.I. Rajput, ibid. 23B, 339 (1984).
- 4 S.N. Suryawanshi and U.R. Nayak, Ind. J. Chem., 18B, 500 (1979).
- 5 Anhyd. NaHCO<sub>3</sub> was used as acid scavenger; under similar conditions, no reaction was observed in the absence of light in each case.

- 6 The products were separated by flash column chromatography; (E)-3 IR: 1650, 1110  $\text{cm}^{-1}$ ; PMR ( $\text{CCl}_4$ ,  $\delta$ ) 1.10, 1.13 (2s, 3H each), 2.53 (br.s, 1H allylic bridgehead and 3.16 (s, 3H, OMe); Mass: m/e 292 (90%,  $\text{M}^+$ ) and 165 (100%); (Z)-3; IR: 1648, 1110  $\text{cm}^{-1}$ ; PMR: 1.16, 1.20 (2s, 3H each), 3.03 (br.s, 1H, allylic bridgehead) and 3.13 (s, 3H, OMe); For E/Z assignments see: U.R.Nayak, T.S.Santhanakrishnan and Sukh Dev, *Tetrahedron* **19**, 2281 (1963); Mass: m/e 292 (90%,  $\text{M}^+$ ), 165 (100%); The E/Z mixture of 3 was reduced (Na/t-BuOH-THF) and subsequently hydrolysed under acidic conditions to a mixture (1:3) of exo and endo aldehydes; IR: 2860 and 1730  $\text{cm}^{-1}$ ; PMR: 0.95, 1.00, 1.06, 1.10 (4s); 2.16 - 2.60 (m, 4H); 9.43, 9.70 (2d) [G. Buchbauer, *Mh.Chem.* **109**, 3 (1978)]. 4 and 5 were isolated as a mixture of E/Z isomers and characterized by direct comparison with authentic samples<sup>3</sup>; 6 was also similarly identified.
- 7 P.J. Kropp, S.A. McNeely and R.D. Devis, *J.Am.Chem. Soc.*, **105**, 6907 (1983).
- 8 In addition to this, a stabilizing influence of the  $\alpha$ -iodo substituent in the intermediate  $\alpha$ -iodo cation in the case of 1 cannot be ruled out.
- 9 Bicyclo (3.2.1) oct-2-ene is reported to have a strain energy six times that of cyclohexane (N.L. Allinger and J.T. Sprague, *J. Am. Chem. Soc.*, **94**, 5734 (1972). However, 5 on treatment with t-BuOK/t-BuOH is reported to undergo ring enlargement and furnish a mixture of t-butyl enol ethers (J. Wolinsky, *J. Org. Chem.*, **26**, 704 (1961).
- 10 Recently, we have observed that iodides I and II also under comparable conditions afford only reduction products to the total exclusion of ionic ones. In spite of the presence of stabilizing  $\alpha$ - $\text{CH}_2$  group, the inability of the rigid tricyclic system to accommodate a bent vinyl cation seems to be responsible for this unusual photobehaviour.

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