

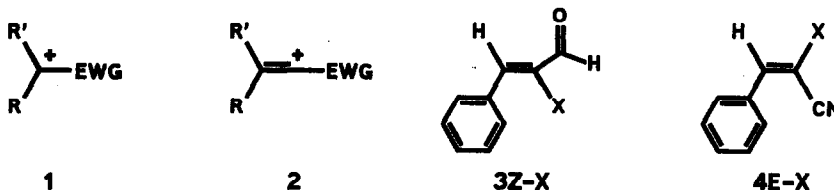
## Photochemical Generation of 'Destabilized' Vinyl Cations

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**Abstract:** Photolysis of  $\alpha$ -formyl and  $\alpha$ -cyano vinyl halides **3Z-X** and **4E-X** (X= Cl or Br) in methanol yields products resulting from the corresponding electronegatively substituted vinyl cations.

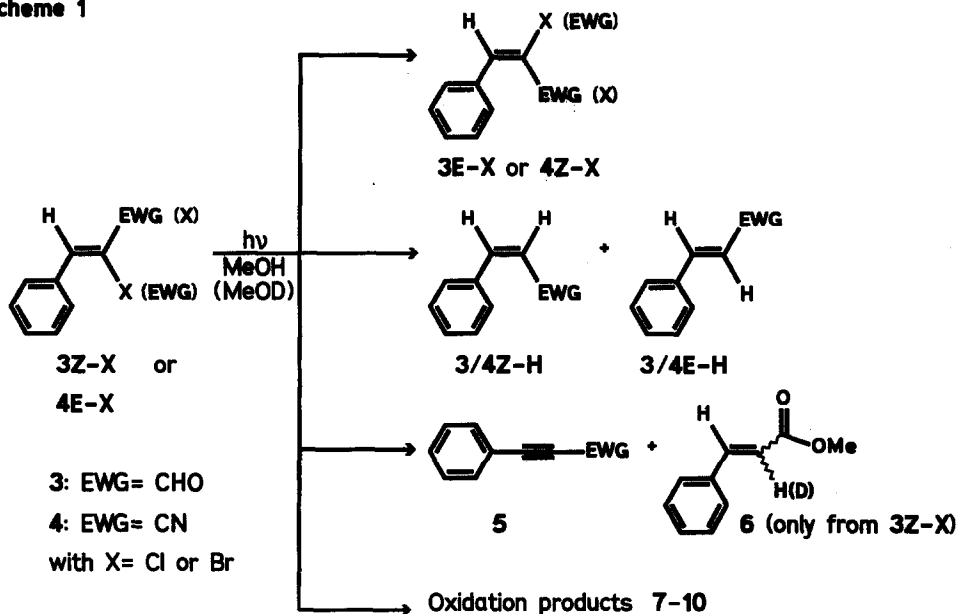
During the past decade carbocations in which the carbon atom formally bearing the positive charge is fitted with an electron-withdrawing group (EWG), have been the focus of considerable attention. Thus far only saturated so-called 'destabilized' carbocations (**1**) have been generated and used for synthetic purposes<sup>1</sup>. We like to report here results which show that the unsaturated analogues **2**, i.e. 'destabilized' vinyl cations, can be generated as well.



As part of our studies<sup>2</sup> of structure-reactivity relationships in the photochemistry of vinyl halides, we have investigated the photochemical behaviour of vinyl halides **3Z-X**<sup>3</sup> and **4E-X**<sup>3</sup> (with X= Cl or Br), substituted with the electronegative  $\alpha$ -formyl (**3**) or  $\alpha$ -cyano (**4**) group. Photolysis, in appropriate media, of vinyl halides with electropositive  $\alpha$ -substituents affords products derived from both vinyl cation and vinyl radical intermediates<sup>4</sup>.

Irradiation of compounds **3Z-X** and **4E-X** in methanol<sup>5</sup> with the light of a high-pressure mercury arc yielded the mixtures of products presented in Scheme 1 and Table 1<sup>7</sup>.

Scheme 1



The formation of phenylacetylenes **5** and methyl cinnamates **6** can be envisioned to occur via the intermediacy of an  $\alpha$ -formyl or  $\alpha$ -cyano substituted vinyl cation (Scheme 2). Expulsion of the  $\beta$ -proton leads to product **5**; the  $\alpha$ -formyl vinyl cation can also expel the 'aldehyde'-proton and give benzyldeneketene. This species reacts with the solvent to yield the esters **6**<sup>8,9</sup>. Use of methanol-OD as solvent resulted in the incorporation (over 80%) of deuterium in product **6**. No nucleophilic substitution products are observed. This is similar to the situation reported for thermally generated saturated carbocations

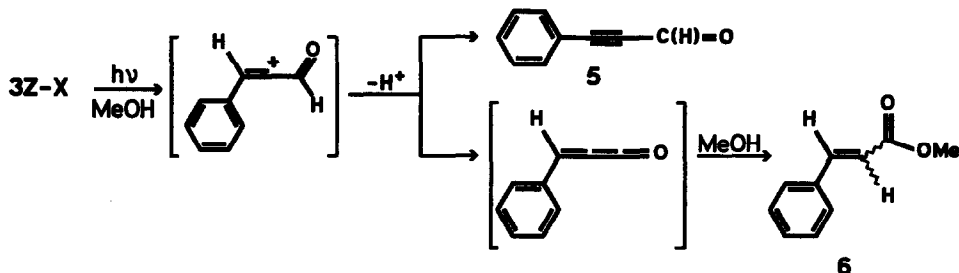
Table 1 Product ratios (%) in the irradiation of 3Z-X and 4E-X in methanol<sup>5</sup>.

RX	3/4Z-X	3/4E-X	3/4Z-H	3/4E-H	5	6Z	6E	7	8	9	10
3Z-Cl	36	37	4	9	2	2	2	2	6		
3Z-Br	30	24	8	21	4	2	2	1	8		
4E-Cl	6	13	24	12	6			5	10	1	14
4E-Br	6	12	20	15	16			7	12	1	9

a: Time of irradiation is 20 minutes for 3Z-X, 4E-Cl and 5 minutes for 4E-Br.

substituted with an  $\alpha$ -cyano group, where also exclusive elimination of a  $\beta$ -proton is found<sup>10</sup>. For  $\alpha$ -carbonyl carbocations it is the major process<sup>11</sup>. The photochemical dehydrohalogenation of alkyl halides has been suggested to occur via 'hot' carbocations<sup>12</sup>.

Scheme 2



Independent generation of the vinyl radicals of 3Z-Br and 4E-Cl, using tri-*n*-butyltin hydride in refluxing toluene with AIBN as initiator<sup>13,14</sup>, resulted in the formation of reductive dehalogenation products 3/4-H (over 80%). No dehydrohalogenation products (5 or 6) were detected. This excludes the possibility that the photo-induced dehydrohalogenation reaction occurs via  $\beta$ -hydrogen atom loss from an intermediate vinyl radical. The alternative of  $H\cdot$  abstraction within a radical-pair formed prior to the formation of the free vinyl and halogen radical can also be excluded. While  $Cl\cdot$  is a better hydrogen abstractor than  $Br\cdot$ , dehydrohalogenation is more efficient with vinyl bromides (Table 1).

The formation of the reductive dehalogenation products Z and E 3-H and 4-H and the oxidation products benzaldehyde (7), benzoic acid (8), methyl benzoate (9) and unidentified 10<sup>15</sup> results from homolytic cleavage of the carbon-halogen bond. The ensuing vinyl radicals abstract a hydrogen atom from the solvent (3/4-H) or react with oxygen (7-10). Exclusion of oxygen increased the yield of reductive dehalogenation products to the same extent as the yield of oxidation products decreased. During the irradiation of 3Z-X and 4E-X also E/Z-isomerization to 3E-X and 4Z-X is observed.

The efficiency of formation of both the vinyl cation- and vinyl radical-derived products depends on the wavelength of excitation. E.g. irradiation of 4E-Cl at  $\lambda_{exc} < 300$  nm gives rise to the formation of all products, whereas the use of  $\lambda_{exc} > 300$  nm only results in E/Z-isomerization. The origin of the wavelength dependence and the scope of the reaction are currently under investigation.

## References and Notes

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3. Compounds **3Z-X** are commercially available. Compounds **4E-X** were synthesized according to a literature procedure: Moore, H.W.; Mercer, F.; Kunert, D.; Albaugh, P.J. *J. Am. Chem. Soc.* **1979**, *101*, 5435-5436.
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5. In the irradiation of the  $\alpha$ -carbonyl vinyl halides (**3Z-X**) sodium bicarbonate was added to the reaction mixture in order to prevent a thermal acid catalyzed formation of dimethyl acetals, due to photoinduced production of formic acid<sup>6</sup>.
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7. No product formation was observed when the reaction mixture was not irradiated.
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13. Neumann, W.P. *Synthesis* **1987**, 665-683.
14. The reaction was carried out under an argon atmosphere to prevent reaction with oxygen. In order to remove most of the oxygen present, toluene was refluxed overnight under argon.
15. GC-MS shows a benzaldehyde-like mass spectrum.

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