Ionic and Radical Pathways in the Photolysis of 1-(4-Chloromethylphenyl)propene

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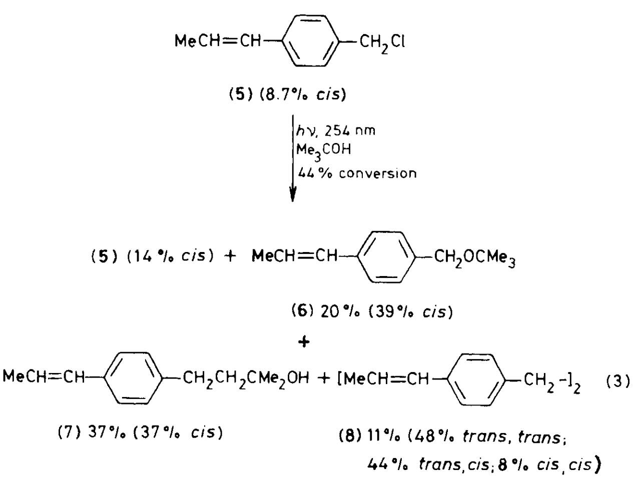
The direct photolysis of 1-(4-chloromethylphenyl)propene (**5**) in t-butyl alcohol affords products derived from both homolytic and heterolytic carbon–chlorine bond fission, whereas triplet sensitized irradiation of (**5**) results only in *cis–trans* isomerization.

The mechanistic details of the photolysis of benzyl chloride (**1**) in nucleophilic media remain unresolved despite having been studied by several research groups in recent years.[1] Many of the reports have been contradictory but the following seems established: both direct and triplet-sensitized irradiation of benzyl chloride (**1**) in alcoholic media afford a mixture of products derived from homolytic and heterolytic cleavage of the carbon–chlorine bond. More interestingly, the products of heterolytic cleavage predominate in the sensitized irradiation whereas the major products obtained on direct irradiation are radical-derived. Equations (1) and (2) show the results of photolysis of (**1**) and t-butyl alcohol.[2]

$$\underset{(1)}{PhCH_2Cl} \xrightarrow[\text{Me}_3\text{COH}\atop 42\%\ \text{conversion}]{h\nu,\ \text{direct}} \underset{(2)\ 30\%}{PhCH_2OCMe_3} + \underset{(3)\ 28\%}{PhCH_2CH_2Ph} + \underset{(4)\ 22\%}{PhCH_2CH_2CMe_2OH} \qquad (1)$$

$$(1) \xrightarrow[\text{Me}_3\text{COH}\atop 42\%\ \text{conversion}]{h\nu,\ \text{acetone}} (2)\ 64\% + (3)\ 18\% + (4)\ 2\% + \underset{10\%}{PhCH_2OH} + \underset{1\%}{PhCH_2CH_2COMe} \qquad (2)$$

The acetone sensitization results define the reactivity of the triplet of (**1**) (evidently T_2 since T_1 is unreactive[1]). By contrast, the singlet state reactivity of (**1**) remains largely



$$(5)\ (trans) \underset{Me_3COH}{\xrightarrow{h\nu,\ xanthone}} (5)\ (cis) \qquad (4)$$

uncharacterized, although a significant portion of the radical products (**3**) and (**4**) obtained on direct irradiation of (**1**) does appear to be singlet-derived.[2] Our wish to investigate benzyl halide singlet state photochemistry led us to study 1-(4-chloromethylphenyl)propene (**5**). Results from the direct and sensitized photolysis of (**5**) are given in equations (3) and (4).

It is seen that (**5**) affords the same type of products on direct irradiation as (**1**). However, in marked contrast to (**1**), triplet sensitization of (**5**) (2.34×10^{-2} M) with xanthone (1.4×10^{-2} M) in t-butyl alcohol resulted solely in *cis–trans* isomerization; no (**6**)—(**8**) could be detected [equation (4)].

The most straightforward interpretation of these results is that products (**6**)—(**8**), obtained on direct irradiation of (**5**), derive from the singlet excited state since the triplet of (**5**), when generated by sensitization, only undergoes isomerization about the double bond. That is, the singlet of (**5**) undergoes both homolytic and heterolytic cleavage of the carbon–chlorine bond with products from the former predominating.† The alternative that some or all of (**6**)—(**8**) arises *via* an upper triplet state of (**5**) cannot be excluded. However, we favour singlet involvement.‡

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† Our results provide no insight into the question of whether (a) the homolytic and heterolytic pathways are completely independent, (b) the heterolysis occurs *via* initial homolytic cleavage of the C–Cl bond and subsequent electron transfer within the caged radical pair (ref. 3), or (c) the products arise *via* an intermediate ion–radical pair (refs. 4—6).

‡ The quantum yield of fluorescence of (**5**) (in cyclohexane) is less than one-tenth that of β-methylstyrene [$\phi_F = 0.028$ (ref. 7)], indicating there is a relatively rapid radiationless process for depleting the lowest singlet excited state of (**5**). One such process could be C–Cl bond cleavage.