Trapping of the Radical Intermediate in the Photochemical Rearrangement of an Allyl Cloride

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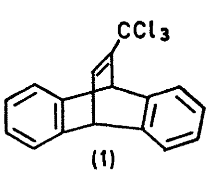
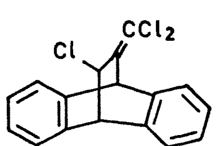
Summary Direct u.v. irradiation of the αβ-unsaturated trichloromethyl compound (**1**) gives the β-chlorodichloromethylene compound (**2**) *via* the intermediate allyl radical (**5**), which can be trapped as the β-bromodichloromethylene compound (**4**) if the reaction is carried out in $BrCCl_3$.

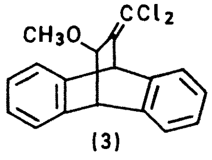
THE mechanism for light-catalysed isomerization of allyl chlorides has been shown to be dependent upon whether the reaction is unsensitized (presumably a singlet reaction)[1] or triplet sensitized.[2] The former is believed to involve free radicals[1] whereas the latter may proceed *via* a vibrationally excited carbonium ion–chloride ion ion-pair.[2]



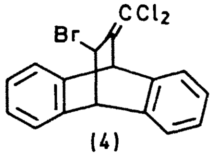
(**1**)



(**2**)



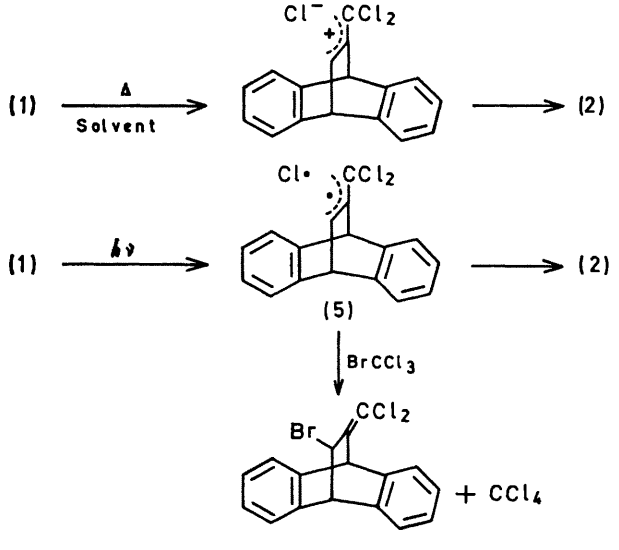
(**3**)



(**4**)

We have previously reported that (**1**) rearranges to (**2**) when irradiated in acetone with a medium-pressure 450w Hanovia type L lamp (Pyrex filter). Direct irradiation in ether or hexane gave a very large amount of what appeared to be polymeric material.[3]

We have irradiated (**1**) (8% solutions under nitrogen) with a sunlamp (G.E. 275w) at 25° in a number of solvent systems [acetone, benzene, carbon tetrachloride, bromotrichloromethane, ether, methanol–tetrahydrofuran (1 : 1)] and find little difference in the overall rate of disappearance



of (**1**) (as followed by ^1H n.m.r. spectroscopy). Irradiation of (**1**) in each of these solvents gave (**2**) accompanied by formation of *ca.* 10—20% of unidentifiable polymeric material. Furthermore, when these irradiations are carried out in the methanol–THF solvent, *ca.* 25% of the product is the previously characterized methyl ether (**3**).[3] However, when (**1**) is allowed to stand in this solvent system at 25° in the dark, (**3**) is formed at essentially the same rate as observed in the photolysis reaction. Also, (**2**) is observed but its rate of formation is much slower than that observed during photolysis. Clearly, the methyl ether (**3**) does not arise from a photochemical reaction but is the product of S_N1 solvolysis of (**1**).[3] Interestingly, photolysis of (**1**) in $BrCCl_3$ gives a mixture of (**2**) [(**2**) is stable under these conditions], and the allyl bromide (**4**)[3] in the ratio of *ca.* 10 : 1. The allyl bromide (**4**) is not present† in the product mixture when (**1**) is heated at 110° (under nitrogen in a sealed tube) in $BrCCl_3$. The thermal isomerization of (**1**) to (**2**) is rather solvent-sensitive and the relative rates of rearrangement follow the order of solvent polarity ($CH_3NO_2 \gg THF > BrCCl_3 \sim CCl_4$).

These results suggest that the thermal reaction (**1**) → (**2**) in solution involves an ion pair,[3] whereas direct irradiation of (**1**) gives rise to the allyl radical (**5**)–chlorine atom radical pair which can recombine to give (**2**) or, if a radical trapping agent ($BrCCl_3$) is present, the allyl radical (**5**) can be scavenged.‡

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† When (**1**) is heated in refluxing $BrCCl_3$ (105°) in the presence of oxygen and benzoyl peroxide, a small amount (<2%) of (**4**) is formed.

‡ Attempts to trap (**5**) with thiophenol failed because thiophenol apparently undergoes an addition reaction with (**1**).

[1] R. W. Phillips and D. H. Volman, *J. Amer. Chem. Soc.*, 1969, **91**, 3418.

[2] S. J. Cristol and G. A. Lee, *J. Amer. Chem. Soc.*, 1969, **91**, 7554.

[3] B. B. Jarvis, *J. Org. Chem.*, 1968, **33**, 4075.