Photolysis of 1-Bromo-2-phenylpropane. A Photochemical Phenyl Migration involving Free Radicals

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Summary The phenyl migration observed when 1-bromo-2-phenylpropane (I) is irradiated is explained by phenyl-bridging during the transition state for energy transfer.

THE irradiation of 1-bromo-2-phenylpropane (I) with u.v. light of wavelength 254 nm in the presence of carbon tetrachloride produces a mixture of 1-chloro-2-phenylpropane (II) and 2-chloro-1-phenylpropane (III). Irradiation of compound (I) with u.v. light of wavelength 313 nm, however, produces only the chloride (II). The reactive intermediate appears to be a free radical as irradiation of compound (I) in n-hexane (either at 254 or 313 nm) produces disproportionation products. Higher molecular weight material was observed in all cases.

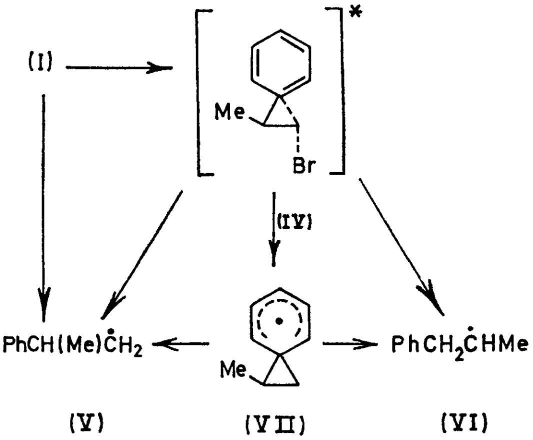
$$\mathrm{PhCH(Me)CH_2Br}\ \mathrm{(I)}\ \xrightarrow[\mathrm{CCl_4\ (1\ mol)\text{–}hexane}]{h\nu\ (254\ \mathrm{nm})}$$

$$\underset{54\%,\ \Phi\,=\,0.00068}{\mathrm{PhCH(Me)CH_2Cl\ (II)}} + \underset{46\%,\ \Phi\,=\,0.00059}{\mathrm{PhCH_2CH(Me)Cl\ (III)}}$$

$$\mathrm{(I)}\ \xrightarrow[\mathrm{CCl_4\ (1\ mol)\text{–}hexane}]{h\nu\ (313\ \mathrm{nm})}\ \underset{\Phi\,=\,0.0012}{\mathrm{(II)}}$$

The irradiations of solutions of compound (I) (0.05 mol) and carbon tetrachloride (1 mol) in n-hexane were performed in either sealed, degassed Pyrex tubes using a Hanovia 450 W medium pressure mercury lamp filtered by a solution of potassium dichromate–sodium carbonate (for 313 nm), or in sealed degassed quartz tubes using a low pressure mercury resonance lamp (for 254 nm). The products were identified by comparison of the retention times for g.l.c. on three different columns and the Raman spectra of the eluted peaks with those of authentic samples of compounds (II) and (III) using a micro-sampling technique.[1] The photolyses were stopped at 1—5% completion to avoid possible complications due to secondary reactions. Formation of the products was proportional to the time of reaction during the period studied.

Irradiation at 254 nm produces a $\pi \rightarrow \pi^*$ transition. The extinction coefficients at 254 nm are 4.4, 236, and 190 for 2-bromobutane, compound (I), and cumene, respectively. Irradiation at 313 nm excites the tail of an absorption band due to a transition involving the bromine atom. Cumene is virtually transparent at 313 nm ($\epsilon < 0.1$) whereas compound (I) absorbs significantly (ϵ 0.74).



The observed rearrangement may result from an internal energy transfer from the phenyl group to the carbon–bromine bond *via* a phenyl-bridged transition state such as (IV) which might decay kinetically to the radicals (V) and (VI). This mechanism is somewhat different from those previously invoked for energy transfer[2] but is analogous to the photorearrangement of 7-phenylhepta-2,4-diene.[3] This mechanism implies that alkyl bromides should quench the fluorescence of alkylbenzenes and we have observed that 2-bromobutane quenches the fluorescence of propylbenzene. A Stern–Volmer treatment indicated that τk_q (the lifetime of the singlet state of propylbenzene × the bimolecular quenching rate constant) is 12 for this process.

The rearrangement may, alternatively, be due to the molecule absorbing more energy at 254 than at 313 nm giving radicals with more vibrational energy in the former than in the latter case. Rearrangement of these 'hot' radicals together with quenching by the solvent might explain the observed wavelength dependence. Photoracemization of optically active hindered biphenyls can occur *via* a vibrationally 'hot' intermediate.[4]

The different results may be due to the reaction of a singlet state at one wavelength and a triplet state at the other This would require that the singlet and triplet states have different probabilities for rearrangement

In the absence of more conclusive evidence, we prefer the first explanation as the large difference in the extent of rearrangement on changing the energy of the incident light seems more compatible with this mechanism

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