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THE PHOTOCHLORINATION OF t-BUTYLBROMIDE

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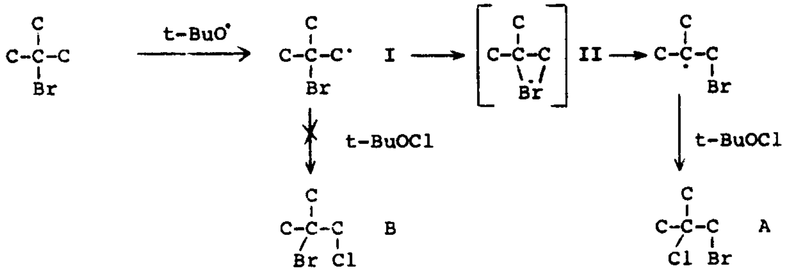
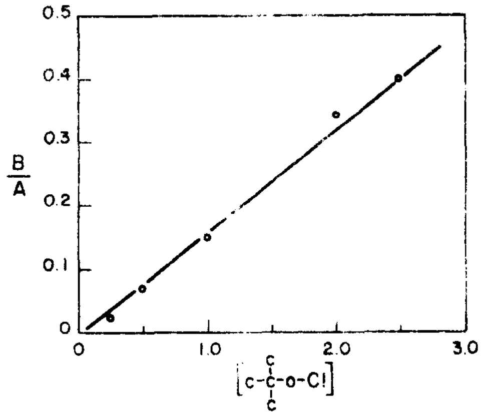
The migration of halogens in halo-alkyl radicals has been the subject of a recent investigation (1,2). 1,2-Bromine migration was invoked to account for the exclusive formation of 1-bromo-2-chloro-2-methylpropane (A) during the chlorination of t-butylbromide with t-butylhypochlorite. The following scheme was suggested (2):



Product B, which would be expected from the intermediate radical I, was not observed. It has also been suggested that a bromine substituent anchimetrically assists in hydrogen abstraction from the neighboring carbon atom during free radical bromination (3) and chlorination (4). In view of these observations it is not clear whether radical I is a true intermediate or if hydrogen abstraction leads directly to a non-classical bridged radical II. Furthermore, recent findings in these laboratories (5) of the behavior of α-bromoalkyl radicals suggested alternate routes to product A. We offer here experimental evidence that a) the classical radical I is indeed an intermediate and b) that the unexpected product A results at least partly from bromine atom elimination from I and readdition to the double bond so formed.

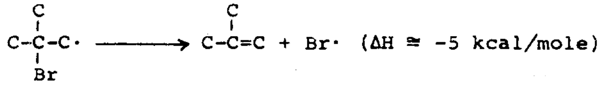
The photochlorination of t-butylbromide with t-butylhypochlorite was carried out at -78°. The kinetic runs were carried out in carbon disulfide as a solvent; other solvents such as Freon 11, Freon 11-CCl_4, or hexafluoroacetone were found to be unsuitable because the reaction mixtures were not homogeneous at -78° at the concentrations desired. Photochlorination yielded the product A as has been previously reported (2). However, the normal product B was always present. Moreover, its proportion in the reaction products increased with increasing hypochlorite concentrations (Fig. I) and reached about 30% in 2.5 M t-butylhypochlorite.

Fig. I Dependence of B/A on t-BuOCl Concentrations



These results demonstrate that the classical radical I is a true intermediate in the photochlorination and can be intercepted via Cl-transfer from t-butylhypochlorite.

The well-known elimination reaction characteristic of α-bromoalkyl radicals (6) is slightly endothermic with an activation energy about equal to the endothermicity (7). However, the elimination reaction of radical I is exothermic with ΔH ≅ -5 kcal/mole, as estimated from bond energy data, and should have a relatively low activation energy. It is therefore expected to be a relatively fast reaction even at -78°.

(a) 

$$\mathrm{C{-}\overset{C}{\underset{Br}{C}}{-}C\cdot} \longrightarrow \mathrm{C{-}\overset{C}{C}{=}C} + \mathrm{Br\cdot} \quad (\Delta H \cong -5\ \mathrm{kcal/mole})$$

Evidence for the occurrence of reaction (a) was obtained from the photochlorination of t-butylbromide at -78° in the presence of allene in concentrations of 1-4 molar. Allene acted as scavenger for free bromine atoms ultimately yielding bromochloropropenes which were obtained in 42% yield (based on the t-butylbromide reacted) at the expense of product A. Direct bromine transfer to allene in a bimolecular step such as

$$\mathrm{C{-}\overset{C}{\underset{Br}{C}}{-}C\cdot} + \mathrm{C{=}C{=}C} \longrightarrow \mathrm{C{-}\overset{C}{C}{=}C} + \mathrm{\dot{C}{-}\underset{Br}{C}{=}C}$$

is unlikely because it has been demonstrated (8) that the dissociation of bromoalkyl radicals is unimolecular and independent of the presence of large concentrations of olefins. In agreement with this we have found that the proportion of bromochloropropenes is not changed by a fourfold change in allene concentration.

Based on the above results compound A is formed, at least in part, along the following sequences:

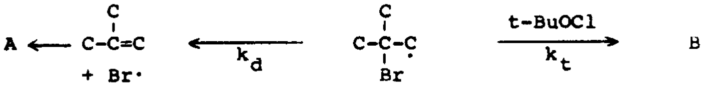
(b)

$$\mathrm{Br\cdot} + \mathrm{C{-}\overset{C}{C}{=}C} \longrightarrow \mathrm{C{-}\overset{C}{\dot{C}}{-}\underset{Br}{C}}$$

(c)

$$\mathrm{C{-}\overset{C}{\dot{C}}{-}\underset{Br}{C}} + \mathrm{t\text{-}BuOCl} \longrightarrow \mathrm{C{-}\overset{C}{\underset{Cl}{C}}{-}\underset{Br}{C}} + \mathrm{t\text{-}BuO\cdot}$$

The proportion of bromine trapped as bromochloropropenes (42%) represents the minimum contribution of reaction (a) toward the formation of A. In view of the very fast addition of Br$\cdot$ to isobutylene, both generated within a solvent cage, its actual contribution may be considerably higher. Assuming product A to result exclusively via sequences (a)-(c), the ratio B/A can be expressed as $B/A = (k_t/k_d)[\mathrm{t\text{-}BuOCl}]$. The ratio of rate constants for chlorine transfer (k_t) and bromine elimination (k_d) as obtained from the slope of Fig. I, is $k_t/k_d = 0.16$ l moles^{-1}



$$\mathrm{A} \longleftarrow \mathrm{C{-}\overset{C}{C}{=}C} + \mathrm{Br\cdot} \xleftarrow[k_d]{} \mathrm{C{-}\overset{C}{\underset{Br}{C}}{-}\dot{C}} \xrightarrow[k_t]{\mathrm{t\text{-}BuOCl}} \mathrm{B}$$

The above results suggest that other proposed 1,2-halogen migrations (1) are also due to halogen atom elimination-readdition sequences.

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