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CHLORINATION OF ALLENE, PROPYNE AND RELATED COMPOUNDS WITH tert-BUTYL HYPOCHLORITE

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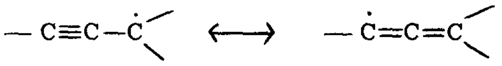
In comparison with the number of investigations concerning the nature of allylic free radicals, there have been relatively few documented studies concerning propargylic free radicals. In principal at least, propargylic radicals can be represented as a hybrid of propargyl and allenic structures, Ia and Ib, but the extent to which either form contributes has been established in only a few instances.



Ia Ib

A study by Collin and Lossing (1) of the C_3H_3 radical obtained in the mercury-photosensitized decomposition of allene and 1, 3-butadiene led these authors to the conclusion that the radical formed in this manner has the propargyl structure Ia. This they established from the fact that the C_3H_3 radical reacted with methyl radicals to give 1-butyne free of 1,2-butadiene. However, the C_3H_3 radical formed in the direct photolysis of 1, 3-butadiene is reported to couple with methyl radicals to give 1-butyne and 1,2-butadiene (2). The e.s.r. spectrum of the C_3H_3 radical has also been reported (3, 4) and has been interpreted in terms of two different hyperfine splitting constants from which the spin densities at the terminal positions were calculated (4). The CH_2 group was found to carry the highest spin density (0. 8), but the spin density at the CH group was far from negligible (0. 6).

The number of investigations of propargylic radicals generated by chemical rather than photochemical means are strictly limited. Walling and co-workers (5) studied the reaction of t-butyl hypochlorite with a number of acetylenes and found the products to be essentially free of chloroallenes. Poutsma and Kartch (6), however, observed the formation of 3-chlorobutyne and 1-chloro-1, 2-butadiene in the photo-induced chlorination of 1-butyne with both molecular chlorine and t-butyl hypochlorite.

We would like to report at this time the results of our work on the chlorination of a number of allenes and acetylenes with t-butyl hypochlorite. Our objectives in this work were to determine the structures of the chlorination products and to infer from these the nature of the radical intermediates involved. We were also interested in determining the relative reactivities of allenic-CH and propargyl-CH towards hydrogen abstraction by the t-butoxy radical.

The chlorination reactions were performed at 0°C using 10:1 mole-ratio of hydrocarbon to t-butyl hypochlorite. The reactants were degassed and sealed under nitrogen in pyrex tubes and irradiated for 2-3 hours with an incandescent light bulb. The reaction mixtures were analyzed by gas chromatography and infrared spectroscopy. Chlorination of both allene and propyne under the conditions described led to the formation of propargyl chloride and t-butyl alcohol as the only major volatile products. A few percent of methyl chloride and acetone were formed, but no chloroallene was detected. That chloroallene was not present was inferred from the absence of a peak in the g. l. c. of the product mixtures having a retention time corresponding to that of authentic chloroallene. Also, the n. m. r. spectrum of the product mixtures showed no resonances attributable to chloroallene. The presence of propargyl chloride was evident from the n. m. r. spectra of the product mixtures and was confirmed by its isolation by preparative g. l. c. and comparison of its infrared spectrum with that of authentic propargyl chloride.

The chain-carrying sequence leading to the observed products is presumably that given in equations 1 and 2.

$$\left.\begin{array}{l} CH_3C\equiv CH + \underline{t}\text{-}BuO\cdot \\ \\ CH_2{=}C{=}CH_2 + \underline{t}\text{-}BuO\cdot \end{array}\right\rangle \longrightarrow C_3H_3\cdot + \underline{t}\text{-}BuOH \qquad (1)$$

$$C_3H_3\cdot + \underline{t}\text{-}BuOCl \longrightarrow ClCH_2C\equiv CH + \underline{t}\text{-}BuO\cdot \qquad (2)$$

The yield of propargyl chloride was however substantially lower than the yield of $\underline{t}$-BuOH (see Table I) which indicates that intermediate C_3H_3 radicals are extensively diverted from the chain transfer step of equation 2. The fate of these radicals, however, is uncertain, and this aspect of the reaction requires further study.

We also investigated the reaction of phenylpropynes and phenylallene with $\underline{t}$-butyl hypochlorite. Chlorination of 3-phenylpropyne gave 3-chloro-3-phenylpropyne, $\phi CHClC\equiv CH$, as the only detectable chlorination product, while chlorination of 1-phenylpropyne gave only 3-chloro-1-phenylpropyne, $\phi C\equiv CCH_2Cl$. Further data is given in Table I. These results are consistent with Walling's earlier finding (5) that the $\underline{t}$-butyl hypochlorite-acetylene reaction produces propargylic chlorides free of chloroallenes.

We made several attempts to chlorinate phenylallene with $\underline{t}$-butyl hypochlorite, but a vigorous reaction occurred instantly on mixing the reagents. G. l. c. analysis of the reaction mixtures revealed at least ten products which we were unable to identify satisfactorily. A dark reaction was also observed between $\underline{t}$-butyl hypochlorite and the phenylpropynes (see also ref. 5). This reaction was slower than the light-induced reaction, but the product composition was the same.

TABLE I

Product and Reactivity Data in t - Butyl Hypochlorite Chlorination

RH	RCl	$\frac{[\mathrm{RCl}]}{[t\text{-BuOH}]}$	$\frac{[\mathrm{RCl}]}{[\phi\mathrm{CH_2Cl}]}$	Reactivity per H
$CH_3C\equiv CH$	$ClCH_2C\equiv CH$	0.41		
$CH_2=C=CH_2$	$ClCH_2C\equiv CH$	0.32		
$\phi C\equiv CCH_3$	$\phi C\equiv CCH_2Cl$	0.56		
$\phi CH_2C\equiv CH$	$\phi CHClC\equiv CH$	0.26		
$CH_3C\equiv CH + \phi CH_3$		0.75	0.49	0.49
$CH_2=C=CH_2 + \phi CH_3$		0.75	0.60	0.45
$\phi C\equiv CCH_3 + \phi CH_3$		0.68	1.6	1.6
$\phi CH_2C\equiv CH + \phi CH_3$		--	5.6	8.4

To obtain an approximate measure of the relative reactivities of the hydrocarbons employed in this study, competitive chlorination experiments were performed using toluene as the standard. The reactions were carried on by allowing equimolar amounts of toluene and hydrocarbon to compete for t -butyl hypochlorite, the total hydrocarbon being in ten-fold excess. The relative yields of benzyl and propargylic chlorides were determined by calibrated g. l. c. and are reported in Table I. If the radicals produced by hydrogen abstraction by t -BuO· suffered no other fate than chain transfer with t -BuOCl, the relative yields of chlorination products could be equated to the relative rates of hydrogen abstraction. Unfortunately, we cannot equate relative rates of abstraction with either the disappearance of hydrocarbon or the formation of chloride since 56% or less of the radicals end up as propargylic chlorides. We therefore regard our reactivity data as qualitative only, but the trends are self-evident and indicate that allene and propyne are slightly less reactive than toluene while the phenylpropynes are more reactive than toluene. Direct competition between

1-phenyl- and 3-phenylpropyne confirmed that 3-phenylpropyne is more reactive. The ratio of $\text{ØCHClC}\equiv\text{CH}$ to $\text{ØC}\equiv\text{CCH}_2\text{Cl}$ was determined as 2.1, although the relative reactivity of the phenylpropynes based on the toluene experiments suggests a larger value of 3.5.

Perhaps the most interesting feature of the competition experiments is that allene and propyne appear to have comparable reactivities. To our knowledge, this is the first evidence from reactivity studies that the vinylic CH bond of allene is of comparable strength to the propargyl CH bond of propyne. The bond dissociation energies of allene and propyne have in fact been determined from electron impact studies as 81.2 and 82.8 kcal. per mole, respectively (7).

In summary, our results indicate that hydrogen abstraction from allene, propyne, 1-phenyl- and 3-phenylpropyne lead to radicals which are best described by the propargylic structure Ia in which most of the unpaired electron density resides at the sp^2-hybridized carbon. Further, the rates of abstraction of allenic and propargyl hydrogens are approximately equal.

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