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REACTION OF 3-METHYL-1-BUTYNE AND 3-METHYL-1,2-BUTADIENE WITH t-BUTYL HYPOCHLORITE: PROPARGYL AND METHYLENEALLYL RADICALS

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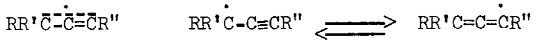
Propargylic radicals have been generated and identified spectroscopically from both acetylenic and allenic precursors (1), and subsequent formation of mixtures of acetylenic and allenic products from such species has been reported (2-4). Thus it is widely accepted, particularly from esr evidence (3a,5), that they are single resonance-stabilized entities (I) rather than mixtures of equilibrating isomers (II). For example, chlorination of either propyne or allene with t-butyl hypochlorite (t-BuOCl) gives only propargyl chloride free from chloroallene and the propargylic and allenic hydrogens were shown to be of comparable reactivity towards t-butoxy radical (6,7). However, it has not been demonstrated, as required by formulation I, that generation of the "same" radical from both acetylenic and allenic precursors gives identical ratios of acetylenic and allenic products in a case where each product is formed in significant and hence readily measurable amounts. We wish to report such an example as well as give information on a related ambident radical system in which free spin is generated adjacent to rather than directly on the allenic linkage.



$$\mathrm{RR'\bar{C}{-}\dot{\bar{C}}{=}\bar{C}R''} \qquad \mathrm{RR'\dot{C}{-}C{\equiv}CR''} \rightleftharpoons \mathrm{RR'C{=}C{=}\dot{C}R''}$$

I II

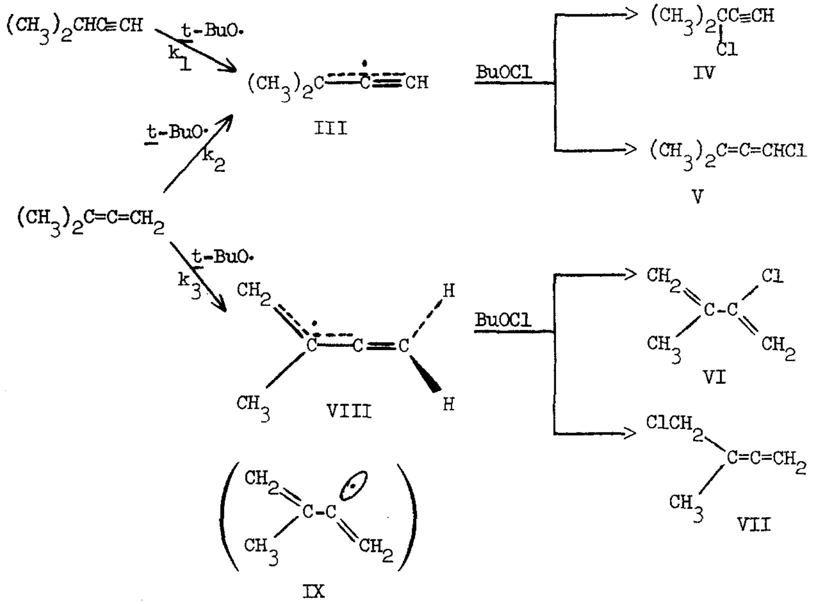
Since propargyl radical (I; R=R'=R"=H) gave no detectable allenic product on reaction with t-BuOCl (6) whereas 1-butyn-3-yl radical (I; R=CH_3, R'=R"=H) gave 8-9% allenic product (4), it seemed reasonable on the basis of our previous observations concerning the influence of methyl groups on propargylic radical reactivity (2) that radical III would give even more allenic product and be a favorable case for study. Photo-initiated reaction of t-BuOCl with excess 3-methyl-1-butyne gave two monochlorides identified as 3-chloro-3-methyl-1-butyne (IV) (8) and 1-chloro-3-methyl-1,2-butadiene (V) (8) in a ratio of 1.7:1.0; (IV + V) accounted for 89% of the t-BuOH produced, a better material balance than generally observed for t-BuOCl-acetylene reactions (6,7). Analogous reaction of the isomeric allene, 3-methyl-1,2-butadiene, gave IV and V in identical ratio along with a third major product, 2-chloro-3-methyl-1,3-

butadiene (VI) (9) such that [(IV + V)/(VI) = 1.4]. A minor product was identified as 4-chloro-3-methyl-1,2-butadiene (VII) (10); the ratio of VI:VII was ~ 15:1. Results are summarized in Table I.

Table I Product and Reactivity Data for t-BuOCl Reactions[a]

RH	t-BuOH (%)[b]	$\frac{\Sigma\ \mathrm{RCl}^c}{t\text{-BuOH}}$	$\frac{IV}{V}$	$k_1^{d,e}$	$k_2^{d,e}$	$k_3^{d,e}$
$(CH_3)_2CHC\equiv CH$	94 ± 4	0.89 ± 0.02	1.72 ± 0.04	13.5 ± 0.7	-	-
$(CH_3)_2C=C=CH_2$	89 ± 2	0.93 ± 0.04	1.73 ± 0.01	-	4.0 ± 0.3	1.05 ± 0.04

[a] Reactions run at 25° with sunlamp initiation; $[RH]_0/[t\text{-BuOCl}]_0$ = 15-25; analyses by glpc. [b] Average of two runs with each RH. [c] Average of two runs with neat RH and three runs with RH-C_5H_{10} mixtures. [d] Average of three runs with RH-C_5H_{10} mixtures; $[RH]_0/[C_5H_{10}]_0$ varied from 0.5 to 2.0. [e] Relative rate constants for abstraction per hydrogen compared to k ≡ 1.00 for a cyclopentyl hydrogen.



The equality of the IV:V ratio from either precursor is consistent with a single propargylic intermediate III; if equilibrating radicals (II) are involved, their interconversion rates would have to be large compared to their rates of reaction with t-BuOCl, a particularly rapid process (11). Products VI and VII are apparently derived from radical VIII formed by abstraction of hydrogen from the methyl group of the allene. Formation of mainly the rearranged product VI demonstrates that the spin in radical VIII is not localized at the methyl carbon but that conjugation with the adjacent π-bond occurs. The presence of a detectable amount of VII suggests that radical VIII (methyleneallylic system) is best pictured as shown with the same geometry as the starting allene; reaction can then occur at either terminus of the "allyl-like" portion to give products VI (initially in a twisted geometry) and VII. Such radicals have been discussed by Kopchik and Kampmeier (12) who calculated by extended Hückel theory that such a p-π conjugated radical should be more stable than the alternative π-π conjugated structure (IX) with diene-like geometry and with the free spin localized on a single carbon atom. Our chemical results do not however rigorously exclude the possibility that IX is more stable than VIII *if* some reaction with *t*-BuOCl occurred to give VII before the 90°-rotation about C_2-C_3 required to convert VIII to IX could take place. Because of the difficulty in measuring the small amount of VII accurately, we have not yet been able to determine if the ratio VI/VII depends on the concentration of *t*-BuOCl.

Relative reactivities of the various hydrogens towards *t*-butoxy radical were measured in competitive reactions with cyclopentane (Table I). The value for the tertiary propargylic hydrogen (k_1 = 13.5 compared to k ≡ 1.00 for a cyclopentyl hydrogen) is essentially the same as that for the corresponding tertiary allylic hydrogen in 3-methyl-1-butene (k = 12.7 on the same scale) (13) but is some 35-fold greater than that for the primary propargylic hydrogen in propyne (6,14). The similar magnitude of k_1 and k_2 again demonstrates (6) the activation of allenic hydrogens towards radical attack compared to ordinary olefinic hydrogens, and the inequality $k_1 > k_2$ is consistent with the greater thermodynamic stability of the allenic precursor (15). The primary hydrogens adjacent to the allenic group are almost identical in reactivity (k_3 = 1.05) to those adjacent to the double bond in isobutylene (k = 0.85) (13) and those adjacent to the triple bond in 2-butyne (k = 0.95) (7).

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