Reduction of Propargylic Chlorides with Tri-*n*-butyltin Hydride. The Ambident Behavior of Propargylic Radicals

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Abstract: Ten substituted propargylic chlorides (**1–10**) have been reduced by tri-*n*-butyltin hydride to produce in each case a mixture of the corresponding acetylene and isomeric allene. Initiation and inhibition studies for a typical case, 3-chloro-3-methyl-1-butyne (**3**), indicated a free-radical reaction course. The initial, kinetically controlled acetylene–allene ratios are thus discussed in terms of the behavior of the series of substituted propargylic radicals toward the stannane as an atom transfer reagent. For those cases (**1**, **2**, **3**, and **6**) in which the free energies of formation of both products are known, increased allene stability compared to the acetylene was paralleled by increased allene formation in the reduction. However, even in cases where the allenic product was thermodynamically the *more* stable isomer (**2** and **3**), acetylenic product was still favored kinetically; this result is related to the greater spin density at the propargylic terminus of the unsymmetrical ambident radical. A search for steric effects in two *t*-butyl-substituted examples (**8** and **9**) was not definitive. The general problem of the factors determining the position of atom transfer to ambident radicals is considered and related to the present results. The reduction of the allenic isomer of **3**, 1-chloro-3-methyl-1,2-butadiene (**11**), did not apparently follow a simple free-radical pathway; hence, this attempt to generate the same propargylic radical from two isomeric parent molecules was foiled.

The species C_3H_3 was first detected by mass spectroscopy from pyrolysis of propargyl iodide at 1000–1100°[1] and from $Hg(^3P_1)$-photosensitized decomposition of allene.[2] This "propargyl radical" has generally been considered to be a resonance hybrid of propargylic structure A and allenic structure B. Attempts to decide which structure more closely resembles the actual delocalized radical have been made based

$$\underset{\text{A}}{\dot{C}H_2C{\equiv}CH} \longleftrightarrow \underset{\text{B}}{CH_2{=}C{=}\dot{C}H}$$

both on physical and chemical data.

Several workers[3-5] have reported esr spectra of propargyl radical trapped in solid matrices; however, under these conditions, lines are broad and assignment of coupling constants is not straightforward. A well-resolved isotropic spectrum was observed by Fessenden and Schuler[6] in the liquid phase from high-energy irradiation of a solution of allene in propane; splitting constants of 18.9 and 12.6 Gauss for the CH_2 and CH groups, respectively, were observed. Spin densities have been related to coupling constants in delocalized radicals by use of the relationship $\alpha = Q\rho$ where α is the observed splitting, ρ is the spin density, and Q is the proportionality constant.[7] By use of $Q \simeq 23$ G, the observed splitting constants give spin densities of 0.82 and 0.55 for the CH_2 and CH groups.[5] However, these values may be distorted in the direction of too much spin density at the allenic terminus since it has been suggested[8] that Q is a function of the hybridization state of carbon with $Q_{sp} > Q_{sp^2}$. To a first approximation, propargyl radical would have sp^2 hybridization at the propargylic terminus and sp hybridization at the allenic terminus with cylindrical symmetry and unequal bond lengths.[9] Spin densities of 0.70 and 0.31 have been assigned from a matrix spectrum[4] based on $Q_{sp^2} = 23.7$ G and $Q_{sp} = 34.7$ G. Thus, although the exact values of spin densities are in doubt, esr spectra do demonstrate greater spin density on the propargylic carbon atom (structure A).

The perturbing effect of added alkyl groups on the distribution of spin between the termini is less clear. Spectra of 1-butyn-3-yl radical (C) have been reported[4,5]

$$\underset{\text{C}}{HC{=}\dot{C}{-}\dot{C}HCH_3} \qquad \underset{\text{D}}{CH_3\dot{C}{=}\dot{C}{-}CH_2}$$

and spin densities of 0.505 and 0.205 assigned[4] to the termini; this represents a relative increase of spin density (0.505/0.205 > 0.70/0.31) toward the site of methyl substitution. However, interpretation of this matrix spectrum ignored all anisotropic effects. A spectrum for the complimentary case, 2-butyn-1-yl radical (D), has been reported[10] but not interpreted.

Several authors[2,6,11] have reported on the coupling of propargyl radicals with methyl radicals and the general consensus is that more 1-butyne than 1,2-butadiene is formed. However, the allenic product in this case is thermodynamically more stable than the acetylenic product,[12] and it has been concluded therefore that the radical resembles structure A and that radical coupling occurs at the site of maximum spin density.[2] However, coupling of 1-butyn-3-yl (C) and methyl radicals has been reported[11b] to give more allenic product than acetylenic product even though

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(7) H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).
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(9) G. Giacometti, *Can. J. Chem.*, **37**, 999 (1959).
(10) V. I. Smirnova, T. S. Zhuravleva, D. N. Shigorin, E. P. Gracheva, and M. F. Shostakovskii, *Russ. J. Phys. Chem.*, **38**, 246 (1964).
(11) (a) R. Srinivasan, *J. Amer. Chem. Soc.*, **82**, 5663 (1960); I. Haller and R. Srinivasan, *ibid.*, **88**, 3694 (1966); (b) P. Kebarle, *J. Chem. Phys.*, **39**, 2218 (1963).
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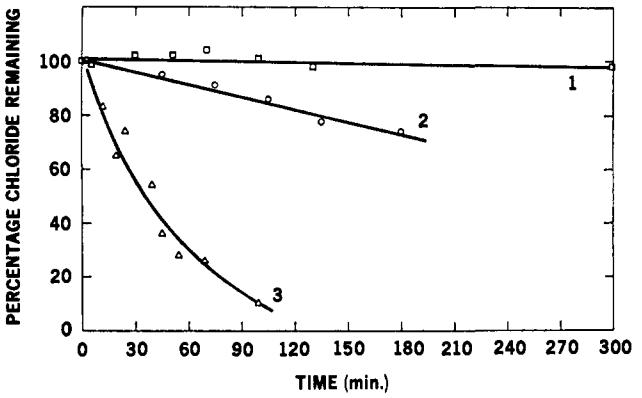

Figure 1. Reaction of 3-chloro-3-methyl-1-butyne (3) with TBTH at 65°: 1 (□), galvinoxyl added; 2 (○) normal reaction; 3 (△), AIBN added.

now the isomers are of essentially equal stability.[12] No unifying theory for such coupling reactions seems apparent in the absence of better data on spin densities.

A variety of substituted propargyl radicals have been allowed to react with atom transfer reagents such as *t*-butyl hypochlorite (BuOCl)[13,14] and chlorine[15] and the major products in all cases have been propargylic rather than allenic derivatives. Chlorination of either propyne or allene with BuOCl gave propargyl chloride as product;[14] the reactivity of the allenic hydrogen in this case supports delocalization in propargyl radical. Reduction of propargyl bromide with tri-*n*-butyltin hydride (TBTH) gave both propyne and allene in a ratio of 5.25:1;[16] by analogy with similar reduction of alkyl halides,[16,17] this reaction most likely proceeds *via* propargyl radical. The recently reported equilibration of propargyl bromide and bromoallene[18] by hydrogen bromide is postulated to proceed *via* hydrogen abstraction and reaction of the bromopropargyl radical with hydrogen bromide at both termini.

Martin and Sanders[19] generated a series of propargylic radicals by homolytic decomposition of β,γ-acetylenic peresters, but products were not required. Throssell[20] studied the pyrolysis of propargyl bromide and bromoallene by the toluene carrier technique, but again products from the presumed propargyl radical were not determined. Photolysis of liquid propargyl bromide at 2537 Å gave methylacetylene as well as higher molecular weight products considered to arise from reactions of propargyl radical.[21] Reaction of tertiary propargylic chlorides with Grignard reagents in the presence of cobaltous chloride which produces coupling products has been postulated to involve propargylic radicals.[22]

For this study we sought a reaction of propargylic radicals in which a significant amount of allenic product

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(22) T. L. Jacobs and P. Prempree, *J. Amer. Chem. Soc.*, 89, 6177 (1967).

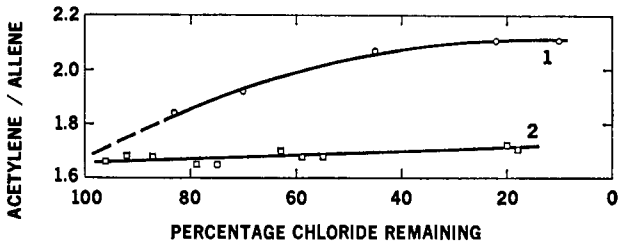

Figure 2. Dependence of product ratio (3a:3b) on extent of conversion for reaction of 3-chloro-3-methyl-1-butyne (3) with TBTH at 65°: 1 (○) AIBN-catalyzed reaction; 2 (□) normal reaction.

was formed so that we could systematically determine the effects of modifying radical structure on the acetylene:allene product ratio. Also, we desired a reaction which specifically generated propargylic radicals to the exclusion of other carbon radicals. Finally, we wished to have products whose relative thermodynamic stability was known. We chose the reduction of propargylic chlorides with TBTH as fulfilling these criteria without excessive experimental difficulty. This paper reports results for reaction of the ten alkylated propargylic radicals derived from chlorides **1–10** with TBTH under kinetically controlled conditions.

Results

Propargylic chlorides **1–10** (Table I) were prepared from the corresponding alcohols by established procedures.[23] Those alcohols which were not commercially available were prepared by reaction of acetylenic Grignard reagents with appropriate ketones. Spectral characteristics of the chlorides are shown in Table I;[24] in most cases these uniquely confirm the structure and in particular rule out the isomeric allenic chloride structure.

Reduction of 3-chloro-3-methyl-1-butyne (**3**) with TBTH was used as a test case to demonstrate the free-radical nature of the reaction. The only volatile products from reduction at 65° with an equimolar amount of hydride were 3-methyl-1-butyne (**3a**) and 3-methyl-1,2-butadiene (**3b**) in 60% yield. Reaction was spontaneous; however, addition of 3 mol % azobisisobutyronitrile (AIBN) gave a marked rate enhancement and addition of 4 mol % of the stable free radical galvinoxyl[25] effectively stopped the reaction (Figure 1). Hydroquinone was not an efficient inhibitor; presumably its ability to scavenge radicals is no better than that of TBTH. For the uncatalyzed reaction, the **3a**:**3b** ratio was independent of extent of reaction from 4 to 82% conversion as determined by direct glpc analysis of reaction mixtures (Figure 2). For the more rapid AIBN-catalyzed reaction, the ratio drifted upward but extrapolated to the same value (1.7 ± 0.1) at zero conversion. The reason for this drift which apparently represents a loss of allene **3b** is not clear since a mixture

$$\underset{\text{3}}{HC{\equiv}C{-}\underset{Cl}{C}{-}(CH_3)_2} \xrightarrow[65^\circ]{Bu_3SnH} \underset{\text{3a}}{HC{\equiv}CCH(CH_3)_2} + \underset{\text{3b}}{H_2C{=}C{=}C(CH_3)_2}$$

(23) G. F. Hennion and A. P. Boisselle, *J. Org. Chem.*, 26, 725 (1961).
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Table I. Spectral Data for Propargylic Chlorides

Structure	Nmr,[a] δ (multiplicity) H-1	H-2	H-2′	H-3	J, cps	Infrared,[b] cm⁻¹ C≡CH	C≡C
$HC\equiv C-CH_2Cl$ (1)[c]	2.24 (t)			3.94 (d)	2.6 (1, 3)		
$HC\equiv C-CHCH_3$ (2), Cl	2.52 (d)	1.73 (d)		4.58 (q,d)	2.5 (1, 3)	3300	2109
					6.9 (2, 3)		
$HC\equiv C-C(CH_3)_2$ (3), Cl	2.51 (s)	1.83 (s)				3300	2111
$HC\equiv C-C(CH_3)(CH_2CH_3)$ (4), Cl	2.51 (s)	1.79 (s)	~1.9 (q)	1.11 (t)	7 (2′, 3)	3300	2112
$HC\equiv C-C(CH_2CH_3)_2$ (5), Cl	2.51 (s)		1.90 (q)	1.12 (t)	7 (2′, 3)	3300	2109
$CH_3C\equiv C-CH_2Cl$ (6)	1.88 (t)			4.22 (q)	2 (1, 3)		2225
$CH_3C\equiv C-C(CH_3)_2$ (7), Cl	1.82 (s)	1.78 (s)					2230
$CH_3C\equiv C-C(CH_3)(t\text{-Bu})$ (8), Cl	1.83 (s)	1.72 (s)		1.15 (s)			2240
$t\text{-BuC}\equiv C-C(CH_3)_2$ (9)[d], Cl	1.21 (s)	1.78 (s)					2210
$C_6H_5C\equiv C-C(CH_3)_2$ (10), Cl	7.28 (m)	1.91 (s)					2209

[a] δ values in parts per million downfield from internal tetramethylsilane in carbon tetrachloride solution (10–20%). [b] Liquid film. [c] Infinite dilution in cyclohexane solution; ref 24a. [d] Reference 22 reports 1.20 (s) and 1.78 ppm (s).

of **3a**, **3b**, TBTH, and AIBN showed negligible reaction under the time and temperature conditions of a typical reduction. AIBN-catalyzed addition of trimethyltin hydride to allenes has been reported at higher temperatures (100° for 9 hr).[26] The starting chloride **3** did not isomerize to allenic isomer during reduction (see below for reactions of this isomer).

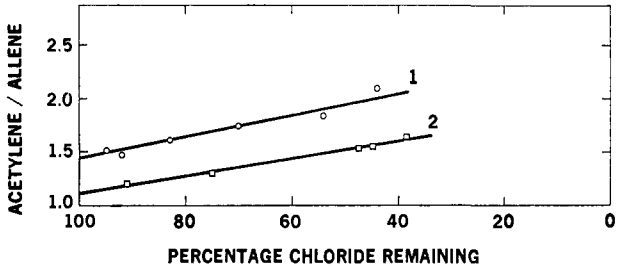


Figure 3. Dependence of product ratios on extent of conversion for reaction of propargylic chlorides with TBTH: 1 (○) 3-chloro-3-methyl-1-pentyne (**4**); 2 (□), 3-chloro-3-ethyl-1-pentyne (**5**).

The other chlorides were then reduced with an equimolar amount of TBTH at 65° to identify products. Volatile products were isolated and, where possible, identified by comparison of their infrared and nmr spectra with those of authentic materials. For those products which were new compounds, identities were established by spectral and elemental analysis and/or by comparison to authentic samples prepared by established routes. In a few cases, identities were assigned from spectra alone but only if there was direct analogy with closely similar, homologous compounds (see Experimental Section). In all cases studied, the only volatile products were the isomeric acetylenes (**1a–10a**) and allenes (**1b–10b**). Spectral data are summarized in Tables II and III. Authentic samples of several of the allenes (**7b–10b**) were prepared from treatment of dibromocyclopropanes with methyllithium by the procedure of Skattebøl.[27]

To determine quantitatively the acetylene:allene ratios, most of the reaction mixtures were subjected to direct glpc analysis periodically during the course of the reduction. Values were extrapolated to zero conversion to obtain the kinetically controlled ratio for those cases where nonconstant ratios were observed (Figure 3).

(26) H. G. Kuivila, W. Rahman, and R. H. Fish, *J. Amer. Chem. Soc.*, 87, 2835 (1965).

(27) L. Skattebøl, *Acta Chem. Scand.*, 17, 1683 (1963).

Table II. Spectral Data for Acetylenes

Structure	Nmr,[a] δ (multiplicity) H-1	H-2	H-3	H-3′	H-4	J, cps	Infrared,[b] cm⁻¹ C≡CH	C≡C
1 2 HC≡C—CH₃ (**1a**)[c]	1.54 (q)	1.66 (d)				2.9 (1, 2)		
1 2 3 HC≡C—CH₂CH₃ (**2a**)	1.77 (t)	2.12 (q, d)	1.17 (t)			2.4 (1, 2) 7 (2, 3)		
1 2 3 HC≡C—CH(CH₃)₂ (**3a**)	1.86 (d)	2.51 (m)	1.18 (d)			2.5 (1, 2) 7 (2, 3)		
3 CH₃ 1 | 2 3′ 4 HC≡C—CH—CH₂CH₃ (**4a**)	1.90 (d)	2.28 (m)	~1.1	~1.4 (m)	~1.1	2.3 (1, 2) ~7 (3′, 4)	3300	2100
1 2 3 4 HC≡C—CH—(CH₂CH₃)₂ (**5a**)	1.92 (d)	2.10 (m)	~1.4		1.00 (t)	2.4 (1, 2) 6.5 (3, 4)	3300	2100
2 CH₃C≡C—CH₃ (**6a**)		1.70 (s)						
1 2 3 CH₃C≡C—CH(CH₃)₂ (**7a**)	1.65 (d)	~2.4 (m)	1.09 (d)			2.5 (1, 2) 7 (2, 3)		
1 2 4 CH₃C≡C—CH—*t*-Bu (**8a**)[d] CH₃ 3	1.71 (d)	~2.1 (m)	1.06 (d)		0.92 (s)	2.5 (1, 2) 7 (2, 3)		2200
1 2 3 *t*-BuC≡C—CH(CH₃)₂ (**9a**)	1.18 (s)	2.47 (7)	1.12 (d)			7 (2, 3)		2210
1 2 3 C₆H₅C≡C—CH(CH₃)₂ (**10a**)	7.23 (m)	2.72 (7)	1.22 (d)			7 (2, 3)		2215

[a] δ values are in parts per million downfield from internal tetramethylsilane in carbon tetrachloride solution (10–20%). [b] Liquid film. [c] Infinite dilution in cyclohexane solution; ref 24b. [d] In benzene solution: $\delta_1 = 1.59$; $\delta_2 = 2.12$; $\delta_3 = 1.09$; $\delta_4 = 0.97$ ppm. [e] Reference 22 reports 1.16 (s), 2.1–2.7 (m), and 1.04–1.16 ppm (d).

Table III. Spectral Data for Allenes

Structure	Nmr,[a] δ (multiplicity) H-1	H-2	H-3	H-4	J, cps	Infrared,[b] cm⁻¹ C=C=C
1 CH₂=C=CH₂[c] (**1b**)	4.55				7	
1 4 3 CH₂=C=CHCH₃ (**2b** ≡ **6b**)	4.55 (m)		1.61 (m)	4.93 (m)		
1 3 CH₂=C=C(CH₃)₂ (**3b**)	4.43 (7)		1.65 (t)		3 (1, 3)	
1 CH₂=C=CCH₂CH₃ (**4b**) CH₃ 3	4.55 (m)					
1 3 4 CH₂=C=C(CH₂CH₃)₂ (**5b**)	4.66 (5)		1.92 (m)	1.03 (t)	3 (1, 3) 7 (3, 4)	1959
2 1 3 CH₃CH=C=C—(CH₃)₂ (**7b**)	4.80 (m)	1.57 (d)	1.63 (d)		2.5 (1, 3) 5 (1, 2)	1970
2 1 4 CH₃CH=C=C—*t*-Bu (**8b**) CH₃ 3	4.92 (m)	1.57 (d)	1.67 (d)	1.05 (s)	~2 (1, 3) 4.5 (1, 2)	1961
2 1 3 *t*-Bu—CH=C=C(CH₃)₂ (**9b**)	4.86 (7)	0.99 (s)	1.65 (d)		3 (1, 3)	1968
2 1 3 C₆H₅CH=C=C(CH₃)₂ (**10b**)	5.93 (7)	7.17 (m)	1.78 (d)		3 (1, 3)	1960

[a] δ values are in parts per million downfield from internal tetramethylsilane in carbon tetrachloride solution (10–20%). [b] Liquid film. [c] Infinite dilution in cyclohexane solution; ref 24b.

In cases where it was not feasible to analyze reaction mixtures periodically (*i.e.*, at low conversion), the allenes were shown to be stable to the reaction conditions in separate control experiments by monitoring the concentration of a given allene present during reduction of chloride **3**. In this way the allene was subjected not only to the temperature and reagents of a typical reduction but also to the chain-carrying radicals. The

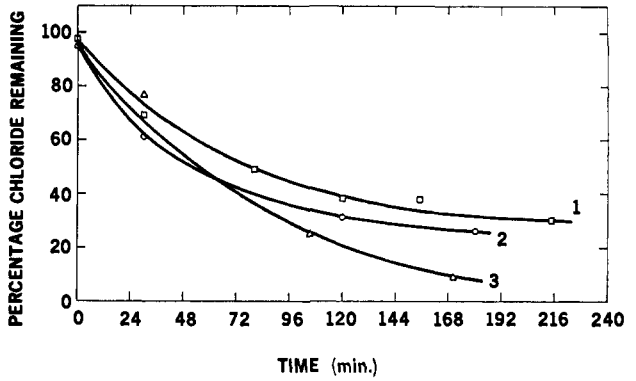


Figure 4. Reaction of 1-chloro-3-methyl-1,2-butadiene (**11**) with TBTH at 65°: 1 (□), galvinoxyl added; 2 (○), normal reaction; 3 (△), AIBN added.

phenyl-substituted allene **10b** was slowly consumed under these conditions and hence only an estimate of the **10a**:**10b** ratio can be made. Acetylene:allene ratios are collected in Table IV; individual details are given in the Experimental Section.

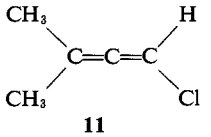
Table IV. Acetylene–Allene Ratios from Reduction of Propargylic Chlorides with TBTH at 65°

$R_1C{\equiv}CC(Cl)R_2R_3 \longrightarrow R_1C{\equiv}CCHR_2R_3 + R_1HC{=}C{=}CR_2R_3$

Series	R_1	R_2	R_3	$R_1C{\equiv}CCHR_2R_3$: $R_1HC{=}C{=}CR_2R_3$	$\Delta\Delta F_f°$ (25°)[a]
1	H	H	H	5.9 ± 0.1	+2.06
2	H	H	CH_3	4.5 ± 0.2	−0.87
3	H	CH_3	CH_3	1.7 ± 0.1	−1.65
4	H	CH_3	C_2H_5	1.4 ± 0.1	
5	H	C_2H_5	C_2H_5	1.1 ± 0.1	
6	CH_3	H	H	25 ± 3	+3.11
7	CH_3	CH_3	CH_3	≥20	
8	CH_3	CH_3	*t*-Bu	10.4 ± 0.3	
9	*t*-Bu	CH_3	CH_3	12.0 ± 1.0	
10	C_6H_5	CH_3	CH_3	>10	

[a] $\Delta\Delta F_f° = \Delta F_f°$(allene) − $\Delta F_f°$(acetylene) from ref 11; a positive value indicates greater thermodynamic stability for the acetylenic isomer.

An attempt was made to reduce 1-chloro-3-methyl-1,2-butadiene (**11**) with TBTH in hopes of generating



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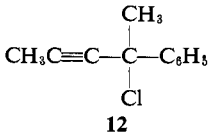

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the same radical as from chloride **3**. However, the rate of reduction was only slightly perturbed by either AIBN or galvinoxyl (Figure 4) and the reaction would appear not to be a clean radical reaction. Four products were detected by glpc analysis: acetylene **3a**, allene **3b**, and two other unidentified compounds of similar glpc retention time. The ratio **3a**:**3b** (~1) was not reproducible and allowing the reaction to proceed to complete consumption of **11** gave only 28% of **3a** + **3b**. The work was not pursued further.

Discussion

The demonstration of both initiation and total inhibition of the reaction of propargylic chlorides and TBTH supports the free-radical chain mechanism anticipated.[16] Thus the acetylene:allene ratios shown in Table IV represent the disposition of the hydrogen in the product-determining hydrogen atom transfer

$$Bu_3SnH + In\cdot \longrightarrow Bu_3Sn\cdot$$

$$Bu_3Sn\cdot + R_1C{\equiv}CC(Cl)R_2R_3 \longrightarrow Bu_3SnCl + R_1\dot{C}{=}\dot{C}{-}CR_2R_3$$

$$R_1\dot{C}{=}\dot{C}{-}CR_2R_3 + Bu_3SnH \longrightarrow Bu_3Sn\cdot + R_1C{\equiv}CCHR_2R_3 + R_1HC{=}C{=}CR_2R_3$$

between the ambident propargylic radical and TBTH. The combination of control experiments on product stability and extrapolation of product ratios to zero conversion identifies these ratios as kinetically controlled.

The product ratios from atom transfer of the more familiar ambident allylic radicals with various reagents have been determined and should serve as models for the present system. During a study of the BuOCl reaction with olefins, Walling and Thaler[28] suggested that the relative energies of the two possible transition states for reaction of an ambident radical would be determined by three, at least in principle, separable factors: (1) odd electron distribution (spin density) in the radical, (2) steric hindrance, and (3) relative product stabilities. The contribution from factor 3 can be evaluated if the two products can be equilibrated or if their free energies of formation are known. In a quantitative sense, the change in $\Delta\Delta F^{\ddagger}$ for the formation of the two possible products as one goes from radical to radical can then be related to the changes in $\Delta\Delta F_f°$ for the two products; *i.e.*, one can convert the product ratios into transition-state energy differences and compare these to product energy differences. Such quantitative treatment has not been carried out for allylic radicals although several qualitative parallels between product ratios and stabilities are known (see below). The steric factor is more nebulous and difficult to define since geometrical factors which interfere with the approach of the atom transfer agent to a particular terminus of the ambident radical will also generally serve to make that particular product more unstable. The spin density (factor 1) was treated[28] by considering the individual effects of adding an alkyl group at a single terminus of the two valence bond forms of allyl radical (E and F). Since an alkyl group is known to stabilize a radical (~4 kcal/mol) more than a double bond (~2 kcal/mol), it was proposed that structure G would now be more stable than struc-

$$\underset{\text{E}}{\dot{C}H_2{-}CH{=}CH_2} \longleftrightarrow \underset{\text{F}}{CH_2{=}CH{-}\dot{C}H_2}$$

$$\underset{\text{G}}{CH_3\dot{C}H{-}CH{=}CH_2} \longleftrightarrow \underset{\text{H}}{CH_3CH{=}CH{-}\dot{C}H_2}$$

ture H and therefore that, in the actual resonance hybrid, spin density would be greater adjacent to the methyl group. However, this argument may be oversimplified since an alkyl group "stabilizes" spin on an adjacent carbon atom not by concentrating it but by delocalizing some of it into the alkyl group by hyperconjugation. Esr spectra can in principle give the desired spin densities, but even then there is an ambiguity as to how spin delocalized on, *e.g.*, the hydrogens at C-4 in structure G affects reactivity at C-3.

(28) C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, 83, 3877 (1961).

For the BuOCl reaction with 1- and 2-olefins, 1-chloro-2-olefin predominates over 3-chloro-1-olefin[28] in accord with the product stability and steric arguments but in opposition to the spin density factor *if* indeed the valence bond argument outlined above that an alkyl group is spin attracting is correct. A large number of reagents have been added to butadiene by a radical mechanism; in all cases except oxygen (see below) the intermediate allylic radical reacts to give predominantly the more stable 1,4 addition product.[29] In particular, addition of thiols to substituted 1,3-butadienes has been shown to give the more stable product (more highly alkylated double bond in all cases).[30a] In contrast to these reactions of substituted allylic radicals with reagents such as BuOCl,[28] thiols,[30a] chlorine,[31] etc., only reaction with oxygen, a key step in the cooxidation of dienes with thiols,[30b] gives predominantly the less stable isomer by reaction at the carbon bearing the greatest spin density *according to* the valence bond argument. It was suggested[30b] that the more the transition state resembled the starting

$$RSH + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \underset{\text{major product}}{RSCH_2CH{=}CHCH_3}$$

$$RSH + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{O_2} \underset{\text{major product}}{RSCH_2\underset{\displaystyle OOH}{\underset{|}{C}}HCH{=}CH_2}$$

radical, the greater would be the contribution from factor 1, spin density; conversely, the more it resembled products, the greater would be the effect of factor 3, product stability. Thus spin density should be expected to make its greatest contribution in the oxygen reaction for which the activation energy is nearly zero and hence a minimum of reorganization has occurred at the transition state. As the activation energy increases, the transition state should undergo more and more structural changes in the direction of products and the contribution from product stability should increase. Hence a dependence of product ratio for a given ambident radical on the nature of the atom transfer agent should be expected.[32]

In consideration of the propargylic series in Table IV, it is instructive to consider first the examples **6**, **1**, **2**, and **3** where the radicals bear only methyl groups so that steric effects should be minimal. Allene formation is seen to be favored by the presence of alkyl groups at the propargylic carbon of the radical and by the absence of alkyl groups at the allenic carbon. For this series, the free energies of formation of the products are known[12] (Table IV) and the product ratios can be seen to parallel product stability in a relatively smooth fashion. For the extreme cases **6** and **3**, $\Delta F_f°$(allene) $-$ $\Delta F_f°$(acetylene) changes by a factor of 4.76 kcal/mol whereas $\Delta\Delta F^{\ddagger} = 2.3RT$ log [acetylene/allene] changes by a factor of 1.80 kcal/mol; thus in the absence of other effects, we can speak of a transition state in which almost one-half of the ultimate difference in product stability has manifested itself.

However, product stability cannot be the sole factor involved because, for cases **2** and **3**, acetylenic product predominates even though it is the *less* stable product. There is thus an obvious kinetic preference for acetylene formation superimposed on product-stability control which must be related to the greater spin density at the propargylic carbon in the parent radical (see introductory section). However, whether or not the relative shifts in spin density *within the set* **6**, **1**, **2**, and **3** are parallel to or in opposition to the observed ratios is a more difficult question. The valence bond approach[28,30] does not parallel the observed results and leads to the conclusion that spin density is a minor factor working in opposition to but swamped out by product stability. Interpretation[4] of the matrix esr spectra of C and D (see introductory section) supports the hypothesis that a methyl group is spin attracting. However, a companion study of the isoelectronic radicals I and J suggested[33] that the methyl group was spin repelling. Therefore we suggest that liquid

$$\underset{\text{I}}{N{=}\dot{C}{-}CH_2} \qquad \underset{\text{J}}{N{=}\dot{C}{-}CHCH_3}$$

phase esr spectra of a series of alkylated propargylic radicals will be required to settle this problem conclusively.

Comparison of cases **3**, **4**, and **5** in which successive replacement of methyl groups by ethyl groups at the propargylic terminus shifts atom transfer more and more to the allenic terminus might suggest a steric effect, but the differences are too small to be conclusive. Similarly, the fact that the ratio from **8** is smaller than that from **7** is as expected for steric interference by the *t*-butyl group with attack at the propargylic terminus. However, comparison of **9** with **7** gives the opposite conclusion. The only safe conclusion therefore is that steric effects for radicals bearing the extent of substitution considered in this study are small.

The predominance of acetylenic isomer from chloride **10** in which the phenyl group is conjugated with the triple bond seems reasonable when compared with chloride **7**. The preparation of 4-chloro-4-phenyl-2-pentyne (**12**) was attempted because the acetylene from this chloride would not have been conjugated with phenyl whereas the allene would have been. Unfortunately, all attempts to convert the corresponding alcohol to **12** were unsuccessful.

Data are available for reaction of a single propargylic radical, 1-butyn-3-yl (C), with three different transfer agents: chlorine, TBTH, and BuOCl; the ratios of propargylic:allenic products were 3.8, 4.5, and 11, respectively.[15] For parent propargyl radical, BuOCl also gives more nearly exclusively propargylic isomer than does TBTH. In the 1-butyn-3-yl series the allenic isomer is the more stable for the hydrocarbons and, although thermodynamic data are not available, the allenic isomer is probably even more stable compared to the propargylic isomer for the chlorides.[34] Hence, all three atom transfers reported

(29) See references in M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966); in C. Walling and E. S. Huyser, *Org. Reactions*, 13, 91 (1963); and in F. W. Stacey and J. F. Harris, *ibid.*, 13, 150 (1963).

(30) (a) A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Amer. Chem. Soc.*, **84**, 3897 (1962); (b) A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *J. Org. Chem.*, **27**, 2439 (1962); A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *ibid.*, **28**, 2355 (1963).

(31) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 2172 (1965).

(32) This quite reasonable interpretation based on the thiol cooxidation system does not explain a more recent claim that coupling of methylallyl and perdeuteriomethyl radicals gives predominantly the *more* stable product: R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **69**, 194 (1965).

(33) T. S. Zhuravleva, Y. S. Lebedev, and V. F. Shuvalov, *J. Struct. Chem. USSR*, **5**, 724 (1964).

exhibit kinetic control to give the thermodynamically unstable isomer. Toward alkyl radicals, chlorine is probably a more reactive atom transfer agent (lower E_a) than BuOCl,[35] and several recent results[36] imply that TBTH is even less reactive than BuOCl as judged by the ability to trap one of a pair of equilibrating radicals. The acetylene:allene ratio order for 1-butyn-3-yl (BuOCl > TBTH > Cl_2) is then not parallel to the probable relative rates of the transfer reactions (TBTH < BuOCl < Cl_2). Also from the preceding discussion of allylic radicals, one might have expected to find the most (rather than the least) propargylic product from the chlorine reaction whose transition state should have resembled the radical the most and the products the least. Obviously, more data are required to understand the factors influencing the reaction of a given ambident propargylic radical with a series of atom transfer agents.[37]

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were recorded on a Beckman IR 10 spectrometer. Nmr spectra were recorded on a Varian A-60 spectrometer in carbon tetrachloride solution, and results are expressed in parts per million downfield from internal tetramethylsilane. Glpc analyses were performed on a Micro-Tek GC 2500 instrument with a thermal conductivity detector and Perkin-Elmer "R" columns (poly(propylene glycol)); areas were determined from the product of peak height and half-width; isomeric acetylenes and allenes were assumed to give equal molar response.

Tin Hydrides. Tri-*n*-butyltin hydride (TBTH) and triphenyltin hydride were prepared by lithium aluminum hydride reduction of the tin chlorides (Matheson Coleman and Bell) and distillation.[38]

Propargylic Alcohols. 3-Butyn-2-ol (**2c**), 2-methyl-3-butyn-2-ol (**3c**), 3-ethyl-1-pentyn-3-ol (**5c**), and 2-butyn-1-ol (**6c**) were obtained from Farchan Research Laboratories; 3-methyl-1-pentyn-3-ol (**4c**) was obtained from K & K Laboratories. To 1.0 mol of freshly prepared ethylmagnesium bromide in 500 ml of anhydrous ether at room temperature was added a solution of 56 g (1.4 mol) of propyne (Matheson) in 600 ml of ether over a 2-hr period. The mixture was stirred 1 additional hr at which time gas evolution had ceased. The mixture was cooled to 0° and 58 g (1.0 mol) of acetone was added with stirring over a 1.5-hr period. The mixture was stirred 0.5 additional hr and allowed to stand overnight before hydrolysis with ice-cold, dilute hydrochloric acid. The separated ether layer was dried ($MgSO_4$) and evaporated. Distillation of the residue gave 30 g (31%) of 2-methyl-4-pentyn-2-ol (**7c**) as a colorless liquid, bp 76–79° (84 mm) [lit.[39] bp 80–81° (100 mm)]. The same procedure with propyne, ethylmagnesium bromide, and methyl *t*-butyl ketone gave 2,2,3-trimethyl-4-hexyn-3-ol (**8c**) (71%), bp 50° (0.6 mm) [lit.[40] bp 68° (13 mm)]. Analogous condensation of *t*-butylacetylene (Farchan Research Laboratories), ethylmagnesium bromide, and acetone gave 2,5,5-trimethyl-3-hexyn-2-ol (**9c**) (31%): bp 83–86° (60–65 mm); mp 31° [lit.[41] bp 85° (60 mm); mp 32°]. 4-Phenyl-2-methyl-3-butyn-2-ol (**10c**), mp 52.5–53.5° (from heptane) [lit.[42] mp 51° (from ether)], was prepared in analogous fashion (55% yield) from phenylacetylene (Farchan Research Laboratories), ethylmagnesium bromide, and acetone.

Propargylic Chlorides. 3-Chloropropyne (**1**, propargyl chloride) was obtained from K & K Laboratories. 3-Chloro-1-butyne (**2**), bp 69–71° (lit.[43] bp 69°), was prepared in 20% yield from 35 g (0.5 mol) of 3-butyn-2-ol (**2c**), 60 g (0.5 mol) of thionyl chloride, and 3.3 g of pyridine; the infrared spectrum was free from allenic absorption and the material was homogeneous to glpc analysis. 1-Chloro-2-butyne (**6**) was prepared from 2-butyn-1-ol (**6c**) and phosphorus trichloride.[44] The tertiary chlorides **3–5**, **7–10** were prepared by treating the alcohols with ice-cold, concentrated hydrochloric acid in the presence of calcium chloride, cuprous chloride, and copper bronze by the method of Hennion and Boisselle.[23] Thus were obtained in uncomplicated fashion 3-chloro-3-methyl-1-butyne (**3**, 50%), bp 74.5–75.5° (lit.[23] bp 74.5–75.5°); 3-chloro-3-methyl-1-pentyne (**4**, 52%), bp 51.5–53°(121–126 mm) [lit.[23] bp 53–56° (128 mm)]; 3-chloro-3-ethyl-1-pentyne (**5**, 62%), bp 61–64° (81 mm) [lit.[23] bp 70–72° (100 mm)]; 4-chloro-4-methyl-2-pentyne (**7**, 56%), bp 83° (215 mm) [lit.[39] bp 61–62° (100 mm)]; 2-chloro-2,5,5-trimethyl-3-hexyne (**9**, 54%), bp 58–61° (36–41 mm) [lit.[41] bp 80–81° (100 mm)]. The product from alcohol **8c** had bp 25–26° (0.5–0.4 mm) but contained ~20% impurity, presumably the isomeric allene. Redistillation gave the desired 4-chloro-4,5,5-trimethyl-2-hexyne (**8**) in 20% yield, bp 51–55° (4.2 mm) [lit.[40] bp 56–57° (8 mm)].

Anal. Calcd for $C_9H_{15}Cl$: C, 68.12; H, 9.53; Cl, 22.34. Found: C, 67.91; H, 9.62; Cl, 22.26.

3-Chloro-3-methyl-1-phenyl-1-butyne (**10**, 50%) had bp 86° (15 mm) but was not stable for extended periods. It tended to lose hydrogen chloride so that satisfactory elemental analyses could not be obtained. Spectral properties of freshly distilled material were consistent with the assigned structure. Such behavior of **10** has been observed previously.[13]

Authentic Acetylenes. Propyne (**1a**) was obtained from the Matheson Co. 1-Butyne (**2a**), 3-methyl-1-pentyne (**4a**), and 4-methyl-2-pentyne (**7a**) were obtained from Chemical Samples Co. 3-Methyl-1-butyne (**3a**) and 2-butyne (**6a**) were obtained from Farchan Research Laboratories. 3-Ethyl-1-pentyne (**5a**), 4,5,5-trimethyl-2-hexyne (**8a**), 2,2,5-trimethyl-3-hexyne (**9a**), and 3-methyl-1-phenyl-1-butyne (**10a**) were isolated by preparative glpc of reduction mixtures of the appropriate propargylic chlorides with TBTH (see below). Structures were assigned on the basis of the method of synthesis and infrared and nmr spectra (Table II).

Anal. Calcd for C_9H_{16}: C, 87.02; H, 12.98. Found for **8a**: C, 86.42; H, 13.07. Found for **9a**: C, 86.84; H, 12.84.

Authentic Allenes. Allene (**1b**) was obtained from the Matheson Co. and 1,2-butadiene (**2b**) from Chemical Samples Co. 3-Methyl-1,2-butadiene (**3b** ≡ **6b**) was prepared in 14% yield by the method of Bailey and Pfeifer,[45] bp 39.0–40.5° (lit.[45] bp 40.0–40.2°). 3-Methyl-1,2-pentadiene (**4b**) and 3-ethyl-1,2-pentadiene (**5b**) were isolated from TBTH reductions by preparative glpc (see below) and structures assigned on the basis of infrared and nmr spectra (Table III). 2-Methyl-2,3-pentadiene (**7b**) was prepared from the reaction of methyllithium with 1,1-dibromo-2,2,3-trimethylcyclopropane by the method of Skattebøl[27] and had bp 71–72° (lit.[27] bp 72°). Allenes **8b–10b** were prepared similarly as outlined below.

1,1-Dibromo-2,3-dimethyl-2-*t*-butylcyclopropane. Condensation of ethylmagnesium bromide and methyl *t*-butyl ketone by the method of Whitmore and Laughlin[46] gave 2,2,3-trimethyl-3-pentanol (37%), bp 59–57° (23–18 mm) [lit.[46] bp 76.2–75.8 (41–39 mm)]. Iodine-catalyzed dehydration[46] gave 3,4,4-trimethyl-2-pentene (34%), bp 110.9° (lit.[46] 108.8–109.2°); the nmr spectrum indicated ~10% of the isomeric 2-ethyl-3,3-dimethyl-1-butene. Treat-

(34) For example, K = [methylacetylene]/[allene] = 32 at 25° based on $\Delta\Delta F_f° = 2.06$ kcal/mol (Table IV). Yet propargyl chloride can be isomerized in significant amount to allenyl chloride and $K < 10$ is implied (T. L. Jacobs and W. F. Brill, *J. Amer. Chem. Soc.*, **75**, 1314 (1953)). Also $K' =$ [propargyl bromide]/[bromoallene] has been reported as 2.69 at 135° with $\Delta\Delta F = 0.83$ kcal/mol;[18] E_a values for homolysis of these bromides[20] imply that bromoallene is actually more stable than propargyl bromide.

(35) G. Chiltz, P. Goldfinger, G. Huybrechts, G. Martens, and G. Verbeke [*Chem. Rev.*, **63**, 355 (1963)] give E_a values for chloroalkyl radicals and chlorine; A. A. Zavitsas and S. Ehrenson, [*J. Amer. Chem. Soc.*, **87**, 2841 (1965)] consider E_a values for alkyl radicals and ROCl.

(36) F. D. Greene and N. N. Lowry, *J. Org. Chem.*, **32**, 875, 882 (1967); M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965); C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966).

(37) For example, we have ignored polar effects in the above discussion. The transition state for transfer from TBTH may be polarized oppositely from those for BuOCl and Cl_2.

(38) H. G. Kuivila and O. F. Beumel, Jr., *J. Amer. Chem. Soc.*, **83**, 1246 (1961).

(39) A. I. Zakharova, *Zh. Obshch. Khim.*, **17**, 686 (1947); *Chem. Abstr.*, **42**, 1871 (1948).

(40) A. I. Zakharova and K. N. Dobromyslova, *Zh. Obshch. Khim.*, **20**, 2029 (1950); *Chem. Abstr.*, **45**, 5607 (1951).

(41) G. F. Hennion and T. F. Banigan, Jr., *J. Amer. Chem. Soc.*, **68**, 1202 (1946).

(42) A. I. Zakharova and Z. I. Sergeeva, *Zh. Obshch. Khim.*, **18**, 1322 (1948); *Chem. Abstr.*, **43**, 2182 (1949).

(43) T. L. Jacobs, W. L. Petty, and E. G. Teach, *J. Amer. Chem. Soc.*, **82**, 4094 (1960).

(44) Prepared by Mrs. B. Boulette by the method of M. S. Schechter, N. Green, and F. B. LaForge, *ibid.*, **74**, 4903 (1952).

(45) W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 95 (1955).

(46) F. C. Whitmore and K. C. Laughlin, *J. Amer. Chem. Soc.*, **54**, 4011 (1932).

ment of this olefin with bromoform and potassium *t*-butoxide[27] gave the desired product (56%), bp 61–62° (0.3 mm).

Anal. Calcd for $C_9H_{16}Br_2$: C, 38.05; H, 5.68; Br, 56.27. Found: C, 38.32; H, 5.57; Br, 56.81.

The nmr spectrum showed a quartet (fine structure) at 1.70 ppm and a multiplet centered at 1.17 ppm corresponding to 1 and 15 protons, respectively.

4,5,5-Trimethyl-2,3-hexadiene (8b). Treatment of 1,1-dibromo-2,3-dimethyl-2-*t*-butylcyclopropane with methyllithium[27] gave the allene in 37% yield, bp 42–43° (28 mm), homogeneous to glpc analysis; spectral characteristics (Table III) support the assigned structure.

Anal. Calcd for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 85.80; H, 12.87.

1,1-Dibromo-2,2-dimethyl-3-*t*-butylcyclopropane. Treatment of 2,4,4-trimethyl-2-pentene (K & K Laboratories) with bromoform and potassium *t*-butoxide[27] gave the desired product (67%), bp 65–71° (1.3 mm).

Anal. Calcd for $C_9H_{16}Br_2$: C, 38.05; H, 5.68; Br, 56.27. Found: C, 37.94; H, 5.47; Br, 56.56.

The nmr spectrum showed singlets at 1.14, 1.22, and 1.39 ppm in a ratio of 9:1:6.

2,5,5-Trimethyl-2,3-hexadiene (9b). Treatment of 1,1-dibromo-2,2-dimethyl-3-*t*-butylcyclopropane with methyllithium[27] gave the allene in 72% yield, bp 69° (136 mm), homogeneous to glpc analysis; spectral characteristics (Table III) support the assigned structure.

Anal. Calcd for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 86.94; H, 12.96.

1,1-Dibromo-2,2-dimethyl-3-phenylcyclopropane. 2-Methyl-1-phenylpropene was prepared by dehydration of 2-methyl-1-phenyl-2-propanol (prepared from benzylmagnesium chloride and acetone in 86% yield) by established procedures[47] in 35% yield, bp 68° (9 mm) [lit.[47] bp 78° (16 mm)]. Treatment with bromoform and potassium *t*-butoxide[27] gave the desired product (70%), mp 45.5–46.5° (from methanol).

Anal. Calcd for $C_{11}H_{12}Br_2$: C, 43.45; H, 3.98; Br, 52.57. Found: C, 43.44; H, 4.05; Br, 52.52.

The nmr spectrum showed singlets at 1.20, 1.58, 2.51, and 7.24 ppm corresponding to 3, 3, 1, and 5 protons, respectively.

3-Methyl-1-phenyl-1,2-butadiene (10b). Treatment of 1,1-dibromo-2,2-dimethyl-3-phenylcyclopropane with methyllithium[27] gave a colorless liquid, bp 41–42° (0.25 mm). The product was not stable for prolonged periods and satisfactory elemental analysis was not obtained; infrared and nmr spectra (Table III) support the assigned structure.

1-Chloro-3-methyl-1,2-butadiene (11) was prepared from 2-methyl-3-butyn-2-ol, concentrated hydrochloric acid, cuprous chloride, ammonium chloride, and copper bronze[48] in 26% yield, bp 56° (155 mm) [lit.[48] bp 62° (175 mm)].

General Procedure for Reductions. Typically, 0.01 mol each of propargylic chloride and TBTH were mixed and transferred to a Pyrex tube which was sealed and placed in a bath at 65.0 ± 0.1° for 2–3 hr. No attempt was made to degas the mixtures and, except where noted, no initiator was used. The cooled tube was opened and the volatile components were vacuum distilled at 65° into a cooled nmr tube so as to isolate them from tin compounds. Nmr and infrared spectra were recorded and glpc analyses carried out on this sample to identify the products. For the higher molecular weight chlorides it was more convenient to use triphenyltin hydride because triphenyltin chloride product precipitated and could be removed by filtration; the filtrate was then used for spectral analysis and thus any heating required for distillation was avoided.

Once the products were identified and their glpc characteristics established, all the reductions were repeated with TBTH and a small amount of an internal standard such as benzene to obtain quantitative results. The reaction mixture was divided among several small tubes which were sealed, transferred to the 65° bath, periodically removed over several hours, and immediately quenched in a Dry Ice–acetone bath; the contents were analyzed for acetylene, allene, and remaining chloride by direct injection into the chromatograph or by nmr spectroscopy. The acetylene–allene product ratios were extrapolated to zero reaction time where possible. Detailed procedures for each chloride follow.

Reduction of 3-Chloropropyne (1). Chloride **1** was treated with TBTH in a tube connected to a gas buret. After 3 hr at 65° the collected gas was analyzed by glpc and only two components were found whose retention times and nmr spectra (mixture) were identical with those of authentic propyne (**1a**) and allene (**1b**). A second reaction mixture was prepared and divided among several tubes which were removed from the 65.0° bath at 15-min intervals. Direct injection into the chromatograph gave propyne–allene ratios which extrapolated to a value of 5.9 ± 0.1 at zero reaction time but decreased slightly with increasing conversion.

Reduction of 3-Chloro-1-butyne (2). Reduction in the same fashion gave an evolved gas in the buret which was shown to be a mixture of 1-butyne (**2a**) and 1,2-butadiene (**2b**) by comparison of infrared and nmr spectra with those of authentic samples. Since the two products could not be completely resolved by glpc analysis, the evolved gas from a second experiment was condensed directly into an nmr tube; the ratio of **2a**:**2b** was 4.5 ± 0.2.

Reduction of 3-Chloro-3-methyl-1-butyne (3). Heating **3** with TBTH at 65.0° for 3 hr gave only two volatile products by glpc analysis which were identified as 3-methyl-1-butyne (**3a**) and 3-methyl-1,2-butadiene (**3b**) by co-injection and infrared and nmr spectral comparison to authentic samples. A quantitative experiment gave a ratio of **3a**:**3b** = 1.7 ± 0.1 by direct glpc analysis which did not vary with extent of conversion (Figure 2). The total yield was 60%. A second run conducted with the addition of 3 mol % AIBN proceeded much more rapidly (Figure 1) and gave an increasing product ratio with time (Figure 2); however, extrapolation to zero conversion again gave **3a**:**3b** = 1.7. A third experiment conducted in the presence of 4 mol % galvinoxyl (Aldrich) gave insufficient product for analysis even after 5 hr (Figure 1).

Reduction of 3-Chloro-3-methyl-1-pentyne (4). The two reduction products were collected by preparative glpc and shown to be 3-methyl-1-pentyne (**4a**) and 3-methyl-1,2-butadiene (**4b**) by spectral analysis and, for **4a**, by co-injection with authentic material. After 2 hr, 56% of the starting chloride had disappeared, 87% of which formed **4a** and **4b**; during this time the ratio **4a**:**4b** gradually increased to 2.1 but extrapolated to 1.4 ± 0.1 at zero reaction time (Figure 3). In the presence of 3 mol % AIBN, the reduction gave 83% **4a** and **4b** in 1.5 hr with the ratio **4a**:**4b** = 1.5 ± 0.1 at zero reaction time.

Reduction of 3-Chloro-3-ethyl-1-pentyne (5). 3-Ethyl-1-pentyne (**5a**) and 3-ethyl-1,2-pentadiene (**5b**), identified as in the **4** series above, were produced in a ratio of 1.1 ± 0.1 extrapolated to zero reaction time (Figure 3). After 3 hr the total yield was 61% and the ratio had increased to 1.5. Repetition in the presence of 2 mol % AIBN gave **5a** and **5b** in 71% yield in the ratio of 1.1 ± 0.1 extrapolated to zero reaction time.

Reduction of 1-Chloro-2-butyne (6). Glpc analysis revealed a major product which was isolated and identified as 2-butyne (**6a**) by comparison to authentic material and a minor product which had the same retention time as 1,2-butadiene (**6b**) but was not isolated. The ratio of **6a**:**6b** was 25 ± 3 by glpc analysis.

Reduction of 4-Chloro-4-methyl-2-pentyne (7). Only a single product could be isolated which was identified as 4-methyl-2-pentyne (**7a**) by spectral comparison to and co-injection with authentic material. Glpc analysis revealed no other products under conditions where 5% of 2-methyl-2,3-pentadiene (**7b**) would have been detected as determined with synthetic mixtures of **7a** and **7b**. Allene **7b** was shown to be stable to typical reducing conditions (see below) and thus **7a**:**7b** must be >20.

Reduction of 4-Chloro-4,5,5-trimethyl-2-hexyne (8). Reduction with triphenyltin hydride for 3 hr at 65.0° gave triphenyltin chloride (83%) as a crystalline solid which was removed by filtration. Glpc analysis of the filtrate revealed two peaks in a ratio of 14.7:1.0 with retention times corresponding to 4,5,5-trimethyl-2-hexyne (**8a**) (identified by spectra after collection) and 4,5,5-trimethyl-2,3-hexadiene (**8b**). The nmr spectrum of this filtrate was the appropriate superposition of the individual spectra of **8a** (major) and **8b** (<10%). Reduction with TBTH gave **8a**:**8b** = 10.4 ± 0.2 by glpc analysis which was constant during the 4-hr reaction period. Allene **8b** was shown to be stable to typical reducing conditions (see below).

Reduction of 2-Chloro-2,5,5-trimethyl-3-hexyne (9). The major product from triphenyltin hydride reduction was isolated and shown to be 2,2,5-trimethyl-3-hexyne (**9a**) by spectral and elemental analysis. Glpc analysis revealed a minor product with the same retention time as authentic 2,5,5-trimethyl-2,3-hexadiene (**9b**); the ratio of **9a**:**9b** = 10.5 ± 1 was supported by the nmr spectrum of the total product. Use of TBTH gave **9a**:**9b** = 12.0 ± 1.0 extrapolated to zero reaction time. After 3 hr, the yield was 55% and the ratio was

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13.7. Allene **9b** was shown to be stable to typical reducing conditions (see below).

Reduction of 3-Chloro-3-methyl-1-phenyl-1-butyne (10). Reduction with triphenyltin hydride for 3 hr at 65.0° gave 77% triphenyltin chloride. The nmr spectrum of the filtrate indicated 3-methyl-1-phenyl-1-butyne (**10a**) and starting chloride **10** but no 3-methyl-1-phenyl-1,2-butadiene (**10b**) under conditions where >10% would have been observable. Neither chloride **10** nor allene **10b** were stable to glpc analysis. The nmr spectrum from a TBTH reaction run for 3 hr did reveal allene with **10a**:**10b** >14. Control experiments (see below) showed however that allene **10b** slowly disappeared under typical reduction conditions. A tentative estimate of the initial **10a**:**10b** ratio is therefore >10.

Allene Stability Control Experiments. In a typical experiment, a mixture of 3-chloro-3-methyl-1-butyne (**3**, 0.01 mol), TBTH (0.01 mol), the allene in question (0.0025 mol), and an inert internal standard such as benzene was prepared and divided among several tubes which were sealed and heated at 65.0°. Tubes were removed periodically and analyzed by glpc. For the allenes examined in this manner (**7b**, **8b**, and **9b**) there was no change in their concentration compared to the internal standard over a 2-hr period during which time 30–40% reduction of **3** had occurred.

With allene **10b**, glpc analysis could not be used but the nmr spectrum of an analogous reaction mixture was recorded periodically over a 4-hr period. The percentage **10b** remaining after 0, 30, 60, 90, and 240 min was 100, 89, 85, 81, and 65%.

A mixture of 3-methyl-1-butyne (**3a**, 0.009 mol), 3-methyl-1,2-butadiene (**3b**, 0.009 mol), TBTH (0.007 mol), and AIBN (0.0003 mol) was heated at 65.0° in a sealed tube for 3 hr. Glpc analysis revealed no significant change in the concentration of either **3a** or **3b**

Bromohydrin Formation in Dimethyl Sulfoxide[1]

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Abstract: A number of olefins have been converted to their respective bromohydrins by the use of N-bromosuccinimide (NBS) and moist dimethyl sulfoxide (DMSO). The mechanism of this stereospecific transformation has been elucidated and general trends have been observed. These include (1) Markovnikov orientation of addition in the absence of steric restrictions; (2) failure of the reaction with highly hindered olefins and olefins bearing electron-withdrawing substituents on the double bond; and (3) systems susceptible to carbonium ion rearrangements yield, where comparison is possible, less rearranged product than has been observed under other conditions.

The use of unsymmetrical addends as a probe to delineate the mechanism (or mechanisms) of olefin addition reactions has received wide attention.[2] In particular, much consideration has been accorded the questions relating to the symmetry of the first formed ion in such reactions.[3-6]

Recent reports[5,7] indicate that unsymmetrical olefins, on reaction with a source of positive bromine (*e.g.*, styrene, Figure 1, R′ = H), produce intermediates best described as Ia (unsymmetrical bridging) rather than Ib (symmetrical bridging) or Ic (no bridging).

However, it has been reported[8] that stereospecificity of addition to *cis*-stilbene (Figure 1, R′ = C_6H_5) (presumably *via* Ia–Ic) decreases with increased solvent polarity, implicating a species capable of rotation before reaction Ic.

Results and Discussion

We have examined the addition of the elements of HOBr across the carbon–carbon double bond of a number of olefins (Table I) in aqueous dimethyl sulfoxide (DMSO) (μ = 4.3)[9] utilizing N-bromosuccinimide (NBS), which is readily soluble in this medium, as a source of positive bromine.[10] Although the exact nature of the brominating agent remains undetermined[11-14] it is, nevertheless, clear from our labeling experiments in which there is specific incorporation of

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(2) (a) See, *e.g.*, P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966, and references therein; (b) J. G. Traynham, *J. Chem. Educ.*, **40**, 392 (1963); (c) A. Hassner and C. Heathcock, *Tetrahedron Lett.*, 1125 (1964).

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(10) L. Horner and E. H. Winkelmann in "Newer Methods of Preparative Organic Chemistry," W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1964, p 151 ff.

(11) For a similar problem in the case of aqueous solution, see E. Berliner, *J. Chem. Educ.*, **43**, 124 (1966).

(12) We consider that, initially, the anion A^- is the succinimide anion. It is not impossible, however, that the transfer of Br^+ to the olefin is not accomplished by NBS directly. The observed induction period (see Experimental Section) might be construed as evidence that either H_2OBr^+ and/or $DMSOBr^+$ is the first species formed and/or that Br_2 is formed by the oxidation of DMSO.[13,14] Should this be the case, the anion A^- would be Br^-. We are currently examining the effect of added ion.

(13) The oxidation of DMSO by NBS with the concomitant formation of bromine is in competition with bromonium formation. Indeed, our results do not exclude formation of Br_2 first, followed by this species being utilized as the source of positive bromine. Preliminary indications dictate that bromine might be used under the proper conditions, in place of NBS.[14] Secondly, the bromide ion thus generated would be expected to compete for bromonium ion (or bromocarbonium ion) producing significant quantities of dibromide. The fact that dibromide, although sought, could not be detected, or could be detected in only trace amounts, in any but the indicated reactions, strongly suggests that (1) the reaction of bromonium (or bromocarbonium) ion, in the absence of unusual steric or electronic effects, with DMSO is very fast and that little bromide is formed before the reaction is over and/or (2) that except as noted, bromide does not effectively compete with DMSO in DMSO. We are currently attempting to generate evidence which will enable a decision to be made between these possibilities as well as that which involves displacement of DMSO from the bromodimethylsulfoxonium intermediate by bromide.

(14) C.-T. Chen and M.-Y. Wong, *Bull. Inst. Chem., Acad. Sinica*, 13, 61 (1967); *Chem. Abstr.*, 12581 (1968). We thank Professor D. Swern for bringing this reference to our attention.