Radical Addition of *tert*-Butyl Hypochlorite to Conjugated Enynes[1]

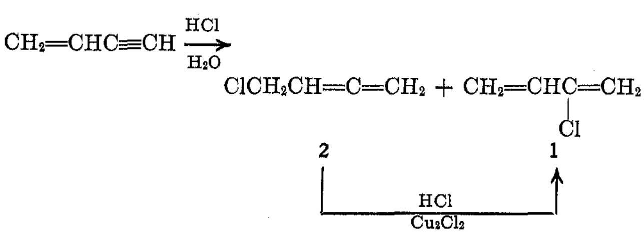
MARVIN L. POUTSMA* AND PEDRO A. IBARBIA

Union Carbide Research Institute, Union Carbide Corporation, Tarrytown, New York 10591

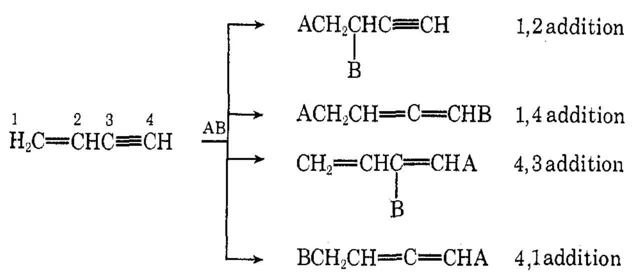
Received May 13, 1970

Radical addition of *tert*-butyl hypochlorite to 1-buten-3-yne (**15**) proceeds by competitive olefinic attack to give 1,2 and 1,4 adducts (**16** and **17**) and acetylenic attack to give a 4,3 adduct (**19**) which suffers rapid secondary electrophilic chlorination to form aldehyde **18**; the former pathway is preferred by a factor of 4 at 25°. Products from the four monomethyl homologs (**6**, **12**, **21**, and **29**) have also been determined and correlated with the intermediacy of ambident radicals. Relative rate comparisons with model hydrocarbons show that *tert*-butoxy radical attack at either terminus of an enyne is enhanced compared to simple olefins and acetylenes. Olefinic attack generates substituted propargylic radicals whose atom transfer behavior is compared to model propargylic radicals. Acetylenic attack seems to generate a resonance-stabilized methyleneallylic radical. For the methylated substrates, small amounts of substitution products were observed.

Since the discovery that chloroprene (1) could be produced commercially by hydrochlorination of vinylacetylene in the presence of cuprous chloride[2a] and the subsequent realization that the kinetically controlled product was largely the isomeric allenic chloride 2,[2b] considerable study has been made of addition reactions of the conjugated enyne linkage.[3] Four modes of addition

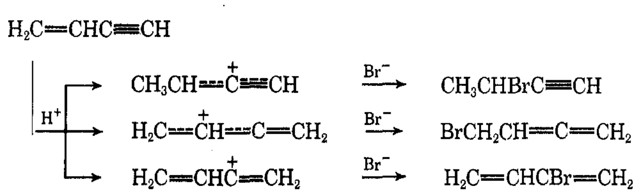


are possible, and examples of all four have been reported.[3] The problem of product distribution can be



separated into three questions for two-step additions: does initial attack occur at the olefinic or acetylenic terminus; what are the ambident properties of the resulting intermediates; and are the kinetically controlled products stable to the reaction and work-up conditions? Since there are often facile anionotropic and prototropic isomerization pathways linking the four product types, it is often difficult to decide whether reported product distributions represent kinetic or thermodynamic control especially in cases where rather severe work-up conditions are involved.

Electrophilic additions have been the most widely studied by use of reagents such as bromine,[4] iodine monochloride,[5] and hydrogen halides.[2,6] Electrophilic attack on vinylacetylene occurs preferentially, but not exclusively, at the acetylenic terminus; the position of attack can however be reversed by the presence of alkyl substituents on the acetylenic terminus of the enyne skeleton. The formation of 1,2, 4,1, and 4,3 adducts from electrophilic addition of hydrogen bromide has been discussed by Cocordano[7] in terms of formation of three separate carbonium ions of comparable energy, two of which are potentially ambident but which were assumed to lead to product formation only at their more positive terminus; molecular orbital calculations were presented to support this formulation.



Addition of alcoholates to give mainly dienyl alkyl ethers,[8] of thiolates to give mainly dienyl alkyl thioethers,[9] and of alkyl lithium reagents[10] represent examples of nucleophilic addition to enynes.

In contrast to heterolytic examples, radical additions to enynes have not been widely studied. In those reported reactions which are probably radical in nature, the experimental systems and conditions were often such that it is difficult to deduce the kinetically controlled product distribution from the data presented. Iodine addition required catalysis by light and gave only 4,3 addition regardless of the substitution pattern of the enyne;[11] however, in view of the usual reversible

* To whom correspondence should be addressed.

(1) Presented in part before the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, Preprints, Division Petroleum Chemistry, p E55.

(2) (a) W. H. Carothers, I. Williams, A. M. Collins, and J. E. Kirby, *J. Amer. Chem. Soc.*, **53**, 4203 (1931); P. S. Bauchwitz, in Kirk-Othmer, "Encyclopedia of Chemical Technology," 2nd ed, Vol. 5, p 215. (b) W. H. Carothers, G. J. Berchet, and A. M. Collins, *J. Amer. Chem. Soc.*, **54**, 4066 (1932).

(3) A. A. Petrov, *Russ. Chem. Rev.*, **29**, 489 (1960); J. H. Wotiz in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, pp 404–411.

(4) N. N. Belyaev, M. D. Stadnichuk, and A. A. Petrov, *J. Gen. Chem. USSR*, **38**, 851 (1968). A. A. Petrov, G. I. Semenov, and N. P. Sopov, *ibid.*, **27**, 1009 (1957). A. A. Petrov and Y. I. Porfir'eva, *ibid.*, **27**, 1872 (1957). A. A. Petrov and Y. I. Porfir'eva, *Dokl. Akad. Nauk SSSR*, **89**, 873 (1953) [*Chem. Abstr.*, **48**, 6373 (1954)]; *Zh. Obshch. Khim.*, **23**, 1867 (1953) [*Chem. Abstr.*, **49**, 147 (1955)].

(5) A. A. Petrov and Y. I. Porfir'eva, *J. Gen. Chem. USSR*, **29**, 2789 (1959).

(6) W. H. Carothers and G. J. Berchet, *J. Amer. Chem. Soc.*, **55**, 2807 (1933); A. A. Petrov and Y. I. Porfir'eva, *J. Gen. Chem. USSR*, **27**, 2132 (1957); J. C. Traynard, *Bull. Soc. Chim. Fr.*, 19 (1962).

(7) M. Cocordano, *ibid.*, 738 (1962).

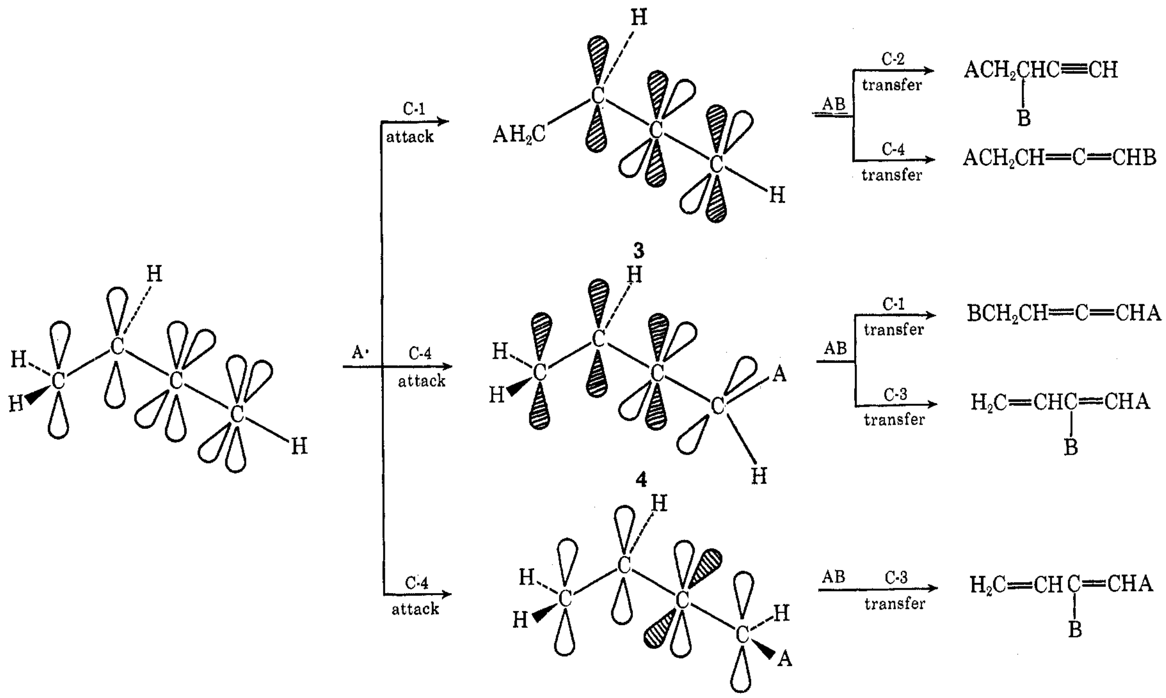
(8) A. Treibs, *Angew. Chem.*, **60**, 289 (1948).

(9) (a) E. N. Prilezhaeva, V. N. Petrov, and A. N. Khudyakova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1042 (1968), and references therein; (b) T. L. Jacobs and A. Mihailovski, *Tetrahedron Lett.*, 2607 (1967).

(10) V. A. Kormer and A. A. Petrov, *J. Gen. Chem. USSR*, **30**, 231 (1960).

(11) A. A. Petrov, Y. I. Porfir'eva, T. V. Yakovleva, and K. S. Mingaleva, *ibid.*, **28**, 2357 (1958).

Scheme I



nature of iodine atom addition, it is dangerous to assume that the observed product is kinetically controlled.

$$\mathrm{RCH{=}CHC{\equiv}CR'} \xrightarrow[h\nu]{I_2} \mathrm{RCH{=}CHCI{=}CIR'}$$

Treatment of several enynes with triphenylmethyl chloride and mercury gave allenic adducts which may have resulted from triphenylmethyl radical addition followed by coupling of the resulting radical with a second triphenylmethyl radical;[12] however, the symmetry does not allow one to decide whether a 1,4 or 4,1

$$\mathrm{CH_2{=}C(CH_3)C{\equiv}CH} \xrightarrow[Hg]{(C_6H_5)_3CCl} \mathrm{(C_6H_5)_3CCH_2C(CH_3){=}C{=}CHC(C_6H_5)_3}$$

addition has occurred. Meerwein arylation of vinylacetylene with aromatic diazonium salts catalyzed by cupric chloride has been reported[13] to give a major 1,2 adduct, a minor 1,4 adduct, and a trace of a 4,3 adduct;

$$\mathrm{CH_2{=}CHC{\equiv}CH} \xrightarrow[CuCl_2]{ArN_2^+Cl^-} \underset{\text{major}}{\mathrm{ArCH_2CHClC{\equiv}CH}} + \underset{\text{minor}}{\mathrm{ArCH_2CH{=}C{=}CHCl}} + \underset{\text{trace}}{\mathrm{CH_2{=}CHCCl{=}CHAr}}$$

alkyl substitution on the enyne caused major shifts in product composition. While it is likely that addition of phenyl radical is the first step in these reactions and that ligand transfer with cupric chloride completes the reaction,[14] it is again rather tenuous to assign kinetically controlled product ratios because yields of adducts seldom exceeded 50% and the individual adducts were not isolated. Addition of aliphatic and aromatic thiols under radical conditions has been reported,[9a,15] but the results are again difficult to interpret because thiyl radical addition may be reversible, the total yield of adducts was low, and unidentified diadducts were observed; the use of excess thiol[15] of course aggravates this latter difficulty. Attempted anti-Markovnikov addition of thiol-

$$\mathrm{CH_2{=}CHC{\equiv}CH + RSH \longrightarrow RSCH_2CH_2C{\equiv}CH + RSCH_2CH{=}C{=}CH_2 + CH_2{=}CHCH{=}CHSR}$$

acetic acid to vinylacetylene did not produce isolable adducts.[16] Szwarc[17] has reported a methyl radical affinity for vinylacetylene of 2.84 compared to 1.00 for styrene but no products are isolated in this technique. If one is willing to take all the reactions just described at face value, then examples of all four modes of addition can be found. However, the mechanistic and experimental ambiguities suggest that such a conclusion would be premature.

Our interest in radical chemistry of enynes is an outgrowth of studies of ambident radicals such as propargyl[18-20] and methyleneallyl.[19] For propargyl radicals we have begun to be able to assess the contributions of such factors as relative product stability, spin distribution in the radical, and nature of the atom transfer agent in determining the ratio of propargylic to allenic products. Radical addition at the olefinic terminus of an enyne should generate a propargylic radical (**3**), whereas addition at the acetylenic terminus should generate one or both of two other unsaturated radicals, the methyleneallylic (**4**) and α-vinylvinylic (**5**) species, the former being also ambident.[19] These possibilities are outlined pictorially in Scheme I (orbitals containing the odd electron are shaded). This formulation is similar to that of Cocordano[7] for the corresponding carbo-

(12) A. F. Thompson, Jr., and D. M. Surgenor, *J. Amer. Chem. Soc.*, **65**, 486 (1943); Y. I. Kheruze and A. A. Petrov, *J. Gen. Chem. USSR*, **31**, 2386 (1961).

(13) A. A. Petrov, K. V. Bal'yan, Y. I. Kheruze, and T. V. Yakovleva, *ibid.*, **29**, 2071 (1959); Y. I. Kheruze and A. A. Petrov, *ibid.*, **30**, 2511 (1960); Y. I. Kheruze and A. A. Petrov, *ibid.*, **31**, 708 (1961).

(14) C. S. Rondestvedt, Jr., *Org. React.*, **11**, 189 (1960); S. C. Dickerman, D. J. Souza, and N. Jacobson, *J. Org. Chem.*, **34**, 710 (1969).

(15) I. G. Sulimov and A. A. Petrov, *J. Org. Chem. USSR*, **2**, 770 (1966).

(16) H. Bader, L. C. Cross, I. Heilbron, and E. R. H. Jones, *J. Chem. Soc.*, 619 (1949).

(17) L. Herk, A. Stefani, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 3008 (1961).

(18) R. M. Fantazier and M. L. Poutsma, *ibid.*, **90**, 5490 (1968).

(19) M. L. Poutsma, *Tetrahedron Lett.*, 2925 (1969).

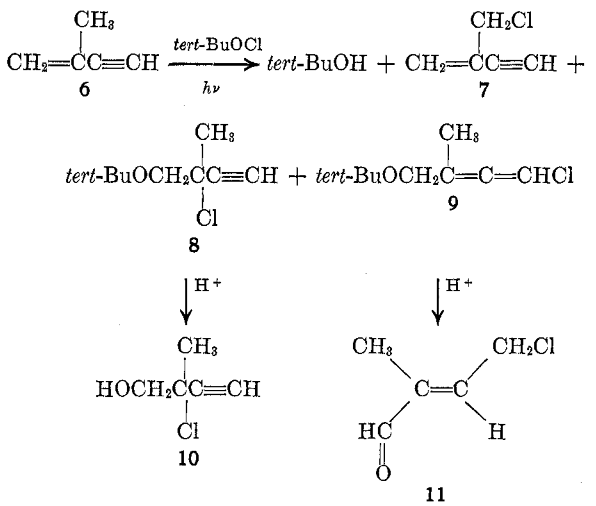
(20) M. L. Poutsma and J. L. Kartch, *Tetrahedron*, **22**, 2167 (1966).

nium ions except that the ambident properties of **3** and **4** are more fully appreciated. The enyne system thus offers the possibility of studying such radicals generated by addition processes and comparing them to model radicals generated by radical substitution processes.[18–20] Also, one should be able to obtain some idea of their relative stability since they are generated from a common precursor.

The following requirements for an addition reagent, AB, were desired: (1) competitive electrophilic addition should be unlikely (thus hydrogen bromide would be a poor choice); (2) the adding radical, A·, should add irreversibly to give a true measure of inherent C-1 *vs.* C-4 attack (thus I· and RS· are questionable); (3) the reagent, AB, should be an efficient atom transfer agent so as to give 1:1 adducts free from telomers; (4) the reaction should proceed under mild conditions to avoid post-reaction isomerization of products; and (5) the products should be amenable to direct glpc or spectral analysis. Our choice to fulfill these requirements was *tert*-butyl hypochlorite (*tert*-BuOCl). One disadvantage is that *tert*-butoxy radical (*tert*-BuO·) has a high tendency to abstract activated hydrogen atoms and hence a certain amount of substitutive chlorination of alkylated enynes was to be expected.

Results

2-Methyl-1-buten-3-yne and *tert*-BuOCl.—2-Methyl-1-buten-3-yne (**6**) was studied first and in most detail. Photoinitiated reaction of *tert*-BuOCl with excess **6** proceeded smoothly at 25° to give, besides *tert*-butyl alcohol (*tert*-BuOH), three products detectable by direct glpc analysis. These were shown by isolation and spectral analysis to be a substitution product [2-(chloromethyl)-1-buten-3-yne (**7**)], a 1,2 adduct [*tert*-butyl 2-chloro-2-methyl-3-butyn-1-yl ether (**8**)], and a 1,4 adduct [*tert*-butyl 4-chloro-2-methyl-2,3-butadien-1-yl ether (**9**)].



The structures of **8** and **9** received additional support from the products of ether cleavages catalyzed by adventitious hydrogen chloride during distillation in which **8** gave 2-chloro-2-methyl-3-butyn-1-ol (**10**) and **9** gave 4-chloro-2-methyl-2-butenal (**11**), presumably with the (*E*) configuration based on nmr spectroscopy.[21] Adduct **8** could be largely isomerized to adduct **9** (with some "residue" formation) by use of cuprous chloride.[22]

Quantitative results derived from glpc analysis are shown in Table I. The adducts **8** and **9** were stable to the analytical conditions as demonstrated with authentic isolated samples. Two disturbing features are apparent when one wishes to draw mechanistic conclusions. First, there is a considerable excess of *tert*-BuOH over **7**. (This disparity is worse for commercially available **6** than for material prepared by us even though glpc analysis showed only trace impurities in the commercial product.) In spite of considerable effort, this point remains unresolved; however, results for other methylated enynes (*vide infra*) suggest that the discrepancy is mainly the result of a loss of **7** or its radical precursor rather than an excess source of *tert*-BuOH. Secondly, the best material balance based on *tert*-BuO groups never exceeded 85%, whereas the *tert*-BuOCl was >95% pure by iodometric titration. (Chlorination of cyclohexane with the same *tert*-BuOCl gave 95% each *tert*-BuOH and cyclohexyl chloride.) One must therefore be concerned whether other adducts have been overlooked or whether adducts **8** and **9** have been consumed in further reaction with *tert*-BuOCl in spite of the large excess of starting enyne. No other adducts which might have arisen from *tert*-BuO· attack at the acetylenic terminus (or further reaction products derived therefrom; *vide infra*) have been found by isolation or direct spectral analysis. No telomeric adducts have been detected either. Also, in separate competitive experiments, adducts **8** and **9** were found to be stable toward *tert*-BuOCl in the dark, adduct **8** was *less* reactive than **6** toward *tert*-BuOCl in the photoinitiated reaction, and adduct **9** was of only comparable reactivity. Hence at the 9.5-fold excess of **6** over *tert*-BuOCl, little consumption of once-formed **8** and **9** in secondary reactions would be anticipated. The lower yields of **8** and **9** at lower ratios of **6**:*tert*-BuOCl is however not surprising. Finally, glpc analysis never showed more than 3–5% acetone, a cleavage product of *tert*-butoxy radical.

TABLE I

REACTION OF 2-METHYL-1-BUTEN-3-YNE (6) WITH *tert*-BUTYL HYPOCHLORITE

			Yields,[a] %			
Entry	$(\mathbf{6})_0/(tert\text{-BuOCl})_0$	Temp, °C	*tert*-BuOH	**7**	**8**	**9**
1[b]	35	25	26.8	3.4	37.4	25.3
2[b]	9.5	25	21.7	3.9	35.5	22.3
3[b]	9.5	25	21.0	3.4	35.7	21.8
4[b]	2.5	25	16.4	1.8	22.9	9.8
5[b]	9.5	0	22.2	2.9	39.6	22.0
6[c]	35	25	38.9	3.0	25.2	16.6
7[c]	9.5	25	41.0	3.0	25.5	16.4
8[c]	9.5	25	30.9	3.2	30.6	19.4
9[c]	2.5	25	34.9	3.3	29.8	13.3
10[c]	9.5	0	40.1	3.3	34.9	20.2
11[c]	9.5	−75	30.4	0.9	38.6	12.6

[a] Yields based on *tert*-BuOCl from glpc results with use of an internal standard. [b] Use of prepared **6** distilled immediately before use. [c] Use of commercially available **6** distilled immediately before use; trace impurity detectable by glpc; at least two extra products formed.

(21) K. C. Chan, R. A. Jewell, W. H. Nutting, and H. Rapoport, *J. Org. Chem.*, **33**, 3382 (1968).

(22) G. F. Hennion, J. J. Sheehan, and D. E. Maloney, *J. Amer. Chem. Soc.*, **72**, 3542 (1950).

TABLE II

COMPETITIVE REACTIONS OF 2-METHYL-1-BUTEN-3-YNE AND CYCLOHEXANE WITH *tert*-BUTYL HYPOCHLORITE AT 25°[a]

$(C_6H_{12})_0/(6)_0$	$(C_6H_{12} + 6)_0/(tert\text{-BuOCl})_0$	Yields,[b] % *tert*-BuOH	7	8	9	$C_6H_{11}Cl$	k_a[c]	k_s[d]
∞	12.7	94.7				94.4		
0.87	14.9	47.9	1.9	25.9	16.0	35.7	12.2	0.19
0.58	15.1	38.4	2.3	24.3	15.2	23.8	11.6	0.22
0.58	15.1	40.0	2.3	24.8	15.0	23.1	12.0	0.23

[a] Using prepared 6. [b] Yields based on *tert*-BuOCl from glpc results with use of an internal standard. [c] Relative rate constant for addition of *tert*-butoxy radical to 6 compared to $k \equiv 1.00$ for abstraction of a cyclohexyl hydrogen based on yield of **8** + **9**. [d] Relative rate constant for abstraction of methyl hydrogens from 6 (per H) compared to $k \equiv 1.00$ for abstraction of a cyclohexyl hydrogen based on yield of **7**.

Results from competitive experiments between **6** and cyclohexane for a limited supply of *tert*-BuOCl to determine the reactivity of **6** toward *tert*-BuO· with respect to addition, k_a, and abstraction, k_s (per H), are shown in Table II. The following equations define k_a and k_s relative to $k \equiv 1.00$ for abstraction of a cyclohexane hydrogen.

$$\frac{k_a}{k} = \frac{[(8) + (9)]}{[(C_6H_{11}Cl)/12]}\,\frac{(C_6H_{12})_0}{(6)_0}$$

$$\frac{k_s}{k} = \frac{[(7)/3]}{[(C_6H_{11}Cl)/12]}\,\frac{(C_6H_{12})_0}{(6)_0}$$

The value of k_s would of course be some fivefold greater if *tert*-BuOH were used as the standard for abstraction and the value of k_a is a minimum subject to the uncertainty in material balance.

1-Penten-3-yne and *tert*-BuOCl.—Analogous reaction with 1-penten-3-yne (**12**) gave only two detectable products: 5-chloro-1-penten-3-yne (**13**) and *tert*-butyl 2-chloro-3-pentyn-1-yl ether (**14**). No allenic adduct was detected and attempts to isomerize **14** under conditions which smoothly converted propargyl chloride **8** to allenyl chloride **9** did not give any detectable new material. Quantitative results are shown in Table III

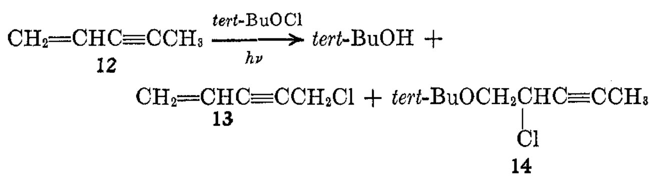


TABLE III

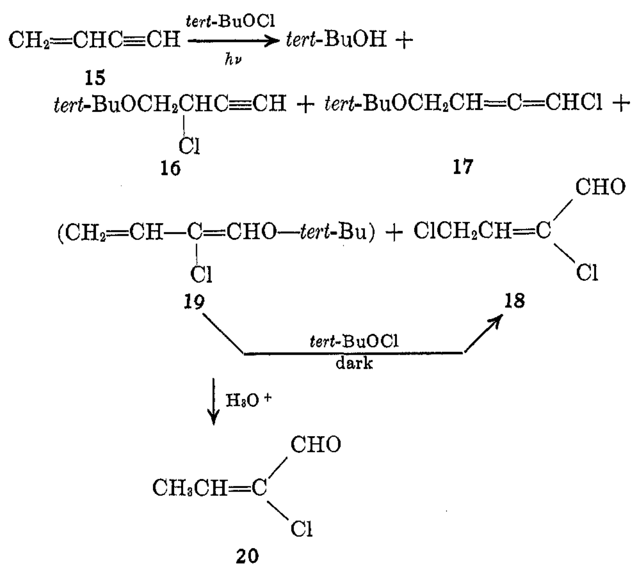
REACTION OF 1-PENTEN-3-YNE (12) WITH *tert*-BUTYL HYPOCHLORITE

Entry	$(12)_0/(tert\text{-BuOCl})_0$	Temp, °C	Yields,[a] % *tert*-BuOH	13	14
1[b]	57.4	25	25.8	18.0	54.6
2[c]	54.3	25	24.6	15.8	47.3
3[b]	53.5	25	25.6	16.5	48.8
4[b]	27.8	25	29.9	20.1	54.9
5[c]	13.4	25	22.8	19.6	52.0
6[b]	13.4	25	26.6	21.1	51.8
7[b]	13.4	0	28.7	19.3	56.4

[a] Yields based on *tert*-BuOCl from glpc results with use of an internal standard. [b] Run with same preparation of **12**. [c] Run with a second preparation of **12**.

and competitive results in Table IV. In this case the balance between *tert*-BuOH and substitution product **13**, while still not exact, was much closer than for enyne **6**. The material balance of *tert*-BuO groups was 75–85%; for runs with very large $(12)_0:(tert\text{-BuOCl})_0$ ratios, the yields values are subject to greater than normal error because of the small quantity of *tert*-BuOCl measured.

1-Buten-3-yne and *tert*-BuOCl.—Analogous reaction with the parent vinylacetylene (**15**) gave, in addition to *tert*-BuOH, four products detectable by glpc analysis. Three of these could be isolated and were identified as *tert*-butyl 2-chloro-3-butyn-1-yl ether (**16**), *tert*-butyl 4-chloro-2,3-butadien-1-yl ether (**17**), and 2,4-dichloro-2-butenal (**18**). The structure of this unexpected aldehyde was confirmed by comparison to an authentic sample prepared by aldol condensation of chloroacetaldehyde.[23] The fourth product (**19**) was detectable only in runs carried to low conversion (<10%), and in preparative runs at higher conversion it had disappeared, apparently with formation of "extra" aldehyde **18**. All attempts to isolated **19** failed and its concentration in the reaction mixture was too low to allow spectral identification. However, acidic hydrolysis of the combined products from several low-conversion runs led to disappearance of **19** and appearance in roughly equivalent amounts of 2-chloro-2-butenal (**20**). Therefore we assign the structure *tert*-butyl 2-chloro-1,3-butadien-1-yl ether to **19**. Such a material would be expected to be very susceptible to electrophilic attack by either a proton or the positive chlorine in *tert*-BuOCl to give an oxygen-stabilized allylic cation which could form an aldehyde group by loss of the *tert*-butyl group.[8]



Quantitative results were obtained in 1,1,2-trichlorotrifluoroethane solvent and are shown in Table V. Again there is excess production of *tert*-BuOH, only an amount equivalent to that of product **18** being predicted

(23) E. Kopp and J. Smidt, *Justus Liebigs Ann. Chem.*, **693**, 117 (1966).

Table IV

Competitive Reactions of 1-Penten-3-yne and Cyclohexane with *tert*-Butyl Hypochlorite at 25°

$(C_6H_{12})_0/(12)_0$	$(C_6H_{12} + 12)_0/(tert\text{-}BuOCl)_0$	Yields,[a] % *tert*-BuOH	13	14	$C_6H_{11}Cl$	k_a[b]	k_s[c]
0.83	27.2	46.0	12.8	33.0	35.4	9.3	1.20
0.52	18.1	43.2	16.4	40.1	25.3	9.8	1.34
0.28	28.4	35.3	15.8	40.9	15.0	9.0	1.16

[a] Yields based on *tert*-BuOCl from glpc analysis with use of an internal standard. [b] Relative rate constant for addition of *tert*-butoxy radical to 12 compared to $k \equiv 1.00$ for abstraction of a cyclohexyl hydrogen based on yield of 14. [c] Relative rate constant for abstraction of the methyl hydrogens from 12 (per H) compared to $k \equiv 1.00$ for abstraction of a cyclohexyl hydrogen based on yield of 13.

Table V

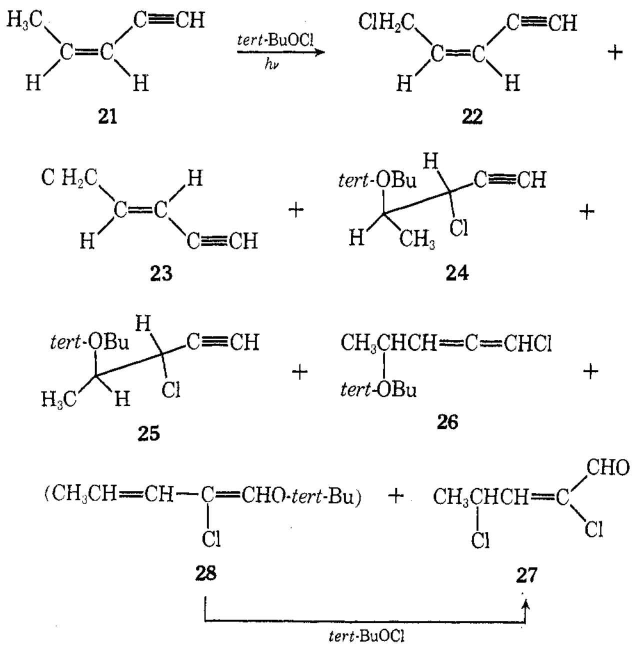
Reaction of 1-Buten-3-yne (15) with *tert*-Butyl Hypochlorite[a]

Entry	Yields,[b] % *tert*-BuOH	16	17	18	19
1	24.9	40.1	3.8	4.7	5.2
2	18.1	39.4	4.3	6.4	5.4

[a] Run at 18–20° with $(C_2F_3Cl_3)_0:(15)_0:(tert\text{-}BuOCl)_0 = 7:3:0.3$ (v/v/v). [b] Yields based on *tert*-BuOCl from glpc results with use of an internal standard.

by the above equation; this anomaly remains. As with the preceding case, the recovery of *tert*-BuO groups in identified products is ~75%.

3-Penten-1-ynes and *tert*-BuOCl.—Reaction of *cis*-3-penten-1-yne (21) gave, besides *tert*-BuOH, seven distinct glpc bands. The first two products were identified as *cis*- (22) and *trans*-5-chloro-3-penten-1-yne (23) which have been reported[24] from a different route. These were followed in retention time by two adducts formed by addition across the double bond. Hydrogenation of the major diastereomeric adduct gave *threo*-*tert*-butyl 3-chloro-2-pentyl ether which had been identified previously as a product from electrophilic chlorination of *cis*-2-pentene in *tert*-butyl alcohol.[25] Therefore we assign the major 1,2 adduct as *threo*-*tert*-butyl 3-chloro-4-pentyn-2-yl ether (24) and the minor 1,2 adduct as the erythro form (25). The fifth product was homogeneous to glpc analysis and was shown to have the gross structure *tert*-butyl 5-chloro-3,4-pentadien-2-yl ether (26).



However, nmr analysis at 100 MHz confirmed the presence of comparable amounts of the two diastereomers possible since the molecule has an asymmetric center adjacent to a dissymmetric allenic group. Still another product was 2,4-dichloro-2-pentenal (27). Finally, only at low conversions, a seventh product (28) appeared which could not be isolated but which, in analogy to the results with vinylacetylene, we assign as *tert*-butyl 2-chloro-1,3-pentadien-1-yl ether.

Parallel reaction with the *trans*- enyne (29) gave the same stable products 22–27 but a different transient (30). Compounds 28 and 30 probably have the same gross structure but differ in configuration around the unsubstituted double bond. Quantitative results are shown in Tables VI and VII. Loss of aldehyde 27 and the unknowns 28 and 30 with increased conversion is clearly more serious than with the previously described substrates. The material balance for *tert*-BuO groups in the highest dilution runs is now excellent (~95%) but the yield of *tert*-BuOH is in considerable excess over the combined yields of 22, 23, and 28 (or 30). Runs with cyclohexane are shown in Table VIII but the results are rather approximate since only a few runs were carried out. Results in Tables VI and VII are presented again in Table IX in terms of a number of ratios of interest for the cis and trans starting materials. The strong dependence of the ratio of products from olefinic attack (24–26) to those from acetylenic attack [27 and 28 (30)] on extent of conversion becomes readily apparent. Note that the cis substitution:trans substitution ratio, the threo:erythro ratio, and the 1,2 adduct:1,4 adduct ratio are essentially the same from either starting material.

Discussion

The results described above are not so exact as might be desired because of the somewhat incomplete material balances, but the uncertainties are hopefully not so large as to obscure the basic pattern of reaction between the methylated enynes and *tert*-butyl hypochlorite as a typical radical addend.

The *position of initial radical attack* as a function of enyne structure is summarized in Table X. Two sets of data are given: the average yields of detectable products at the lowest conversions studied (see Tables I, III, V, VI, and VII) and the k_a values, relative rate constants for addition, derived from competitive runs with cyclohexane (see Tables II, IV, and VIII). Values of k_a for model olefins and acetylenes[26,27] are also listed. The two sets of data vary somewhat for the 3-penten-1-yne cases and the values of k_a for the acetylenic terminus are probably low since the competitive runs were not carried out at as low conversion as the product runs.

(24) I. Bell, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 2597 (1957).

(25) M. L. Poutsma and J. L. Kartch, *J. Amer. Chem. Soc.*, **89**, 6595 (1967).

(26) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

(27) C. Walling, L. Heaton, and D. D. Tanner, *ibid.*, **87**, 1715 (1965).

Table VI

Reaction of *cis*-3-Penten-1-yne (21) with *tert*-Butyl Hypochlorite at 25°

$(21)_0/$ $(tert\text{-BuOCl})_0$	Yields,[a] % *tert*-BuOH	22	23	24	25	26	27	28
52.4	54.2	8.2	6.8	9.2	4.2	7.5	8.9	10.0
13.1	36.2	8.8	6.7	8.7	4.6	7.7	6.7	5.0
4.4	30.0	10.0	7.7	7.7	4.2	6.7	3.1	0.7

[a] Yields based on *tert*-BuOCl from glpc results with use of an internal standard.

Table VII

Reaction of *trans*-3-Pentene 1-yne (29) with *tert*-Butyl Hypochlorite at 25°

$(29)_0/$ $(tert\text{-BuOCl})_0$	Yields,[a] % *tert*-BuOH	22	23	24	25	26	27	30
52.5	56.1	8.5	7.4	6.9	3.6	5.9	10.5	8.9
13.1	44.4	9.0	10.1	6.9	3.5	5.4	8.3	3.9

[a] Yields based on *tert*-BuOCl from glpc results with use of an internal standard.

Table VIII

Competitive Reactions of *cis*- (21) and *trans*-3-Penten-1-yne (29) and Cyclohexane with *tert*-Butyl Hypochlorite at 25°

Isomer	$(C_6H_{12})_0/$ $(21, 29)_0$	$(C_6H_{12} + 21, 29)_0/$ $(tert\text{-BuOCl})_0$	Yields,[a] % *tert*-BuOH	22	23	24	25	26	27	28	30	$C_6H_{11}Cl$	k_a[b]	k_s[c]
21	0.84	24.2	65.1	4.7	2.8	5.8	2.6	4.6	6.1	2.9		42.1	3.1, 2.2	0.6
21	0.42	18.6	42.8	5.5	4.3	5.9	2.5	4.6	2.9	3.8		24.1	2.7, 1.4	0.7
29	0.42	18.7	62.6	5.6	5.9	4.9	2.3	4.4	5.4		1.5	26.9	2.2, 1.3	0.7

[a] Yields based on *tert*-BuOCl from glpc analysis with use of an internal standard. [b] Relative rate constant for addition of *tert*-butoxy radical to enyne compared to $k \equiv 1.00$ for abstraction of a cyclohexyl hydrogen; first value for olefinic terminus based on yield of 24–26; second value for acetylenic terminus based on yield of 27 + 28 (30). [c] Relative rate constant for abstraction of the methyl hydrogens from 21 (29) (per H) compared to $k \equiv 1.00$ for abstraction of a cyclohexyl hydrogen based on yield of 22 + 23.

Table IX

Product Ratios from Reactions of *cis*- (21) and *trans*-3-Penten-1-yne (29) with *tert*-Butyl Hypochlorite at 25° (from Tables VI and VII)

Isomer	$(21, 29)_0/$ $(tert\text{-BuOCl})_0$	(24 + 25)/ (26)	(24 + 25 + 26)/ [27 + 28 (30)]	(24 + 25 + 26)/ (22 + 23)	(24)/ (25)	(22)/ (23)
21	52.4	1.79	1.11	1.39	2.2	1.2
21	13.1	1.75	1.79	1.35	1.9	1.3
21	4.4	1.75	4.89	1.05	1.8	1.3
29	52.5	1.77	0.85	1.03	1.9	1.2
29	13.1	1.93	1.30	0.83	2.0	0.9

Table X

Dependence of Position of *tert*-BuO· Attack on Enyne Structure

Substrate	Olefinic attack % products	k_a[a]	Acetylenic attack % products	k_s[a]
$CH_2{=}CHC{\equiv}CCH_3$	50–55	9.5	...[b]	...[b]
$CH_2{=}C(CH_3)C{\equiv}CH$	60–65	12	...[b]	...[b]
$CH_2{=}CHC{\equiv}CH$	40–45	*c*	10–12	...[c]
cis-$CH_3CH{=}CHC{\equiv}CH$	20–23	2.9	15–20	1.8
trans-$CH_3CH{=}CHC{\equiv}CH$	15–17	2.2	18–20	1.3
$CH_2{=}CHCH_2CH_3$[d]		0.3		
$CH_2{=}CHC_6H_5$[e]		7.0		
$CH_3CH_2C{\equiv}CH$[e]				<0.1[f]

[a] See text for definition. [b] Not detected. [c] Not determined. [d] From ref 26. [e] From ref 27. [f] Based on failure to observe adduct.

However, the k_a values serve to connect the data for the various substrates. *For the parent case, olefinic attack is about four times as facile as acetylenic attack.* To the extent that this difference in transition state free energies (*ca.* 0.8 kcal/mol) reflects the stabilities of the resulting radicals, the propargylic radical produced by olefinic attack is indicated to be slightly more stable than the radical produced by acetylenic attack, but the competition is closely balanced. For radical addition to a series of related substrates, methyl groups substituted at the site of attack sterically retard the rate of attack whereas those substituted at more remote sites where they can stabilize the resulting radical enhance the rate of attack.[28] These effects clearly apply to the enynes, the most noticeable effect being the achievement of as much acetylenic as olefinic attack by substitution of a methyl group at the olefinic terminus.

Addition of *tert*-butoxy radical to the olefinic terminus of vinylacetylene and its analogues with a terminal double bond is some 25 times as rapid as addition to a terminal olefin such as 1-butene.[26] This result supports the resonance-stabilized nature of the resulting propargylic radical. A similar extent of activation of a conjugated double bond has been reported for styrene.[27] In analogous fashion, the triple bond in vinylacetylene (and the 3-penten-1-ynes) is activated by the adjacent double bond compared to an ordinary triple bond.[27] Again a resonance-stabilized radical is implicated (*vide infra*).

(28) W. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 221; C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, Chapters 4, 6, and 7; M. Szwarc and J. H. Binks in "Theoretical Organic Chemistry," Butterworths, London, 1959, p 262.

TABLE XI
AMBIDENT BEHAVIOR OF PROPARGYLIC RADICALS TOWARD *tert*-BuOCl

Radical	Acetylenic:allenic product ratio
tert-$BuOCH_2CH$—C═CCH_3 (**31**)	Large
CH_3CH—C═CCH_3 (**32**)	Large[a]
tert-$BuOCH_2C(CH_3)$—C═CH (**33**)	1.55
$CH_3C(CH_3)$—C═CH (**34**)	1.72[b]
tert-$BuOCH_2CH$—C═CH (**35**)	10
CH_3CH—C═CH (**36**)	12[c]
tert-$BuOCH(CH_3)CH$—C═CH (**37**)	1.8

[a] L. R. Byrd and M. C. Caserio, *J. Amer. Chem. Soc.*, **92**, 5422 (1970). [b] Reference 19. [c] Reference 20.

The *ambident behavior of the propargylic radicals* is shown in Table XI along with that of three model radicals not containing *tert*-butoxy groups. The parent radical in the series (**35**) gives a 10:1 ratio of acetylenic to allenic adducts, essentially identical to the ratio from model radical **36** not containing the *tert*-butoxy group (this may be compared to the reaction with butadiene which gives predominantly a 1,4 adduct[29a]). Radical **35** has recently been observed[29b] by esr from interaction of *tert*-butoxy radical and vinylacetylene at −96°. Previously[18] we have shown that the ratio of acetylenic to allenic product from reaction of a series of methylated propargylic radicals with a different chain transfer agent (tri-*n*-butyltin hydride) responded in an orderly fashion to the relative stabilities of the two products. Since these relative product stabilities are primarily a function of the substitution pattern at the termini of the three-carbon propargylic system, the correspondence in behavior between **35** and **36** is thus reasonable since the *tert*-butoxy group is not in a position to affect directly the relative stabilities of products **16** and **17**. Secondly, the trend of increased allene formation as one goes from **31** to **35** to **33** is exactly as predicted from previous work.[18] Note again the close correspondence between the behavior of **31** and its model **32**, and of **33** and its model **34**. A more surprising result is that from **37** which might have resembled **36** more than **34**. A role of remote steric effects may be appearing in this case.

The same ratio of threo:erythro adducts (**24** and **25**) was obtained from both *cis*- and *trans*-3-penten-1-yne and hence radical **37** must have achieved rotational equilibrium about the C–C bond adjacent to the radical site before reaction with *tert*-BuOCl occurred. The stereoselectivity in these products (**24**/**25** ∼ 2) indicates a favored direction of approach to the radical terminus adjacent to the asymmetric *tert*-BuOCHCH$_3$ group. However, much less, if any, stereoselectivity is observed at the more remote terminus leading to allenic products. Since no cis–trans isomerization of recovered enyne was detected, olefinic attack of the *tert*-BuO· radical must be reversible.

(29) J. K. Kochi, *J. Amer. Chem. Soc.*, **84**, 2785 (1962); (b) J. K. Kochi and P. J. Krusic, *ibid.*, **92**, 4110 (1970).

The structure and behavior of the radicals formed by acetylenic attack on vinylacetylene and 3-penten-1-yne is somewhat less certain because the initial product(s) was not stable to *tert*-BuOCl, but we feel that *dienic product formation (4,3 addition) predominates over allenic product formation (4,1 addition)* because, whereas either of the unsaturated ethers **38** or **39** could have reacted with *tert*-BuOCl to give the observed dichloroaldehydes, the hydrolysis of **19** to give 2-chloro- rather than 4-

RCH═CH—C(Cl)═CHO—*tert*-Bu (**38**)   RCH(Cl)—CH═C═CHO—*tert*-Bu (**39**)

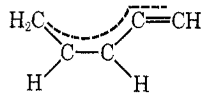
chloro-2-butenal supports a dienic structure for the initial adduct. However, product data alone cannot show whether the actual radical intermediate is best described by the methyleneallylic structure **4** or the α-vinylvinylic structure **5** since **4** may well prefer to give largely dienic product; in fact, generation of a radical adjacent to an allenic bond has been shown[19] to give largely dienic product. The observed enhanced reactivity of the triple bond in the enynes, compared to a simple acetylene, tends to support formation of a resonance-stabilized radical such as **4**. Similar arguments have been proposed[30] to correlate rates of addition of alkyl radicals to phenylacetylenes. Recent esr evidence[29b] also supports structure **4** rather than **5** for the parent C_4H_5 radical.

In retrospect, the results for Meerwein arylation[13] correlate rather well with our results subject to the uncertainties outlined earlier. Thus, olefinic attack predominates for vinylacetylene but significant acetylenic attack can be achieved when an alkyl group is placed on the double bond; also, isopropenylacetylene gives the largest 1,4:1,2 adduct ratio. A 4,1 adduct is claimed as the product of acetylenic attack, contrary to our system, but this structural assignment was based only on ir spectral evidence on the mixed adducts. The products obtained from radical thiol additions[15] also are generally similar except that the propargylic radicals seem to give relatively larger amounts of 1,4 adduct than with *tert*-BuOCl.

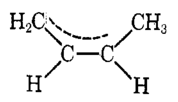
With respect to the substitution products formed by hydrogen abstraction from the methyl groups, relative rate constants found for enynes **12**, **21**, and **29** (k_t = 1.2, 0.7, and 0.7, respectively) are not unreasonable since both primary allylic[26] and primary propargylic[27] hydrogen atoms have been found to be of comparable reactivity to cyclohexane hydrogens (k_t = 1.00) toward *tert*-BuO·. However, the value for **6** based on observed substitution product **7** (k_t ∼ 0.2) seems low and a value based on observed *tert*-BuOH would be more consistent. A second result worthy of note is the failure to maintain stereochemistry in the monochlorides derived from **21** and **29**. Under very similar temperature and concentration conditions, Walling and Thaler[26] found that the allylic radicals derived from *cis*- and *trans*-2-butene were geometrically stable. These contrasting results may suggest that the more extended

(30) G. E. Owen, Jr., J. M. Pearson, and M. Szwarc, *Trans. Faraday Soc.*, **61**, 1722 (1965); M. Gazith and M. Szwarc, *J. Amer. Chem. Soc.*, **79**, 3339 (1957).

conjugation in radical **40** than in radical **41** (using the cis cases as examples) has lowered the barrier to rotation



40



41

about the C_2–C_3 bond. A similar case has been observed by Denney and Hoyle[31] in the crotononitrile series.

Experimental Section

Starting Materials.—2-Methyl-1-buten-3-yne (**6**) from Farchan Research Laboratories was used for all preparative and some quantitative runs after distillation through an 18-in. spinning-band column. However, this material contained a trace impurity detectable by glpc analysis and a second lot of **6**, bp 32–33° (lit.[32] bp 34°), was prepared by dehydration[32] of 2-methyl-3-butyn-2-ol (Farchan); the impurity was now absent. 1-Penten-3-yne (**12**) was prepared by treatment of the tosylate of 3-pentyn-1-ol (Farchan) with aqueous base[33] and distilled through the spinning-band column, bp 59–60° (lit.[34] bp 59.2°). Vinylacetylene (**15**) was prepared from dehydrohalogenation of 1,4-dichloro-2-butene[35,36] and distilled through a 3-ft, vacuum-jacketed, helix-packed column fitted with a condenser through which isopropanol chilled to $\sim -30°$ was circulated. The material was stored over hydroquinone and transferred to the reaction vessel when desired by vaporization and condensation. 3-Penten-1-yne was prepared by treatment of the tosylate of 4-pentyn-2-ol (Farchan) with aqueous base[33] and the individual isomers (**21** and **29**)[37] separated in >99% purity by careful distillation through an annular Teflon spinning-band column. Cyclohexane was distilled from sodium. *tert*-Butyl hypochlorite (*tert*-BuOCl) (Frinton Laboratories) was distilled before use.

Glpc Analyses.—All analyses were performed on a Microtek 2500 R instrument with thermal conductivity detection. For 2-methyl-1-buten-3-yne products, Perkin-Elmer column "B" [bis(2-ethylhexyl) sebacate] was used at 60° to elute starting materials and *tert*-BuOH followed by programming at 10°/min to 120° to complete the analysis. Calibration factors to correct areas to molar amounts compared to the internal standard, chlorobenzene, were determined from authentic mixtures for *tert*-BuOH (1.25), **8** (0.70), **9** (0.75), and chlorocyclohexane (0.98); because of the low yield and instability of **7**, it was not calibrated but a value of 1.05 was used equal to that for similar chloride **13**. For 1-penten-3-yne products, analyses were performed on column "B" programmed from 60 to 128° and calibration factors were determined for both **13** (1.05) and **14** (0.74). For vinylacetylene products, column "B" was used between 60 and 120° and calibration factors were determined for **16** (0.74) and **18** (1.00). Calibration factors of 0.75 were assumed for adducts **17** and **19**; this is probably a rather safe assumption if one considers the similarity of the factors which were determined for other adducts. For the 3-penten-1-yne products, Perkin-Elmer column "O" (silicone grease) was used at 95° to separate all the components except *tert*-BuOH which was determined in a separate analysis on "B." Calibration factors were determined for **22** (1.10), **23** (1.10), **24** (0.75), a mixture of **25** and **26** (0.72, same value used for both), and **27** (1.01). A factor of 0.75 was again assumed for **28** and **30** based on the other similar adducts. Several of the preparative glpc collections for this substrate were performed on Perkin-Elmer column "Q" (Apiezon grease).

Product Identification from Reaction of 2-Methyl-1-buten-3-yne (6) and *tert*-BuOCl.—Photoinitiated reaction (275-W sun lamp through Pyrex) of *tert*-BuOCl with an at least tenfold excess of **6** at $\sim$25° was complete in <1 hr as judged by a negative starch–iodide test. Glpc analysis showed three products of significance, in addition to *tert*-butyl alcohol, labeled A–C in order of increasing retention time. Reactions with a smaller excess of **6** showed additional glpc peaks of retention time greater than C which are apparently the result of secondary reactions.

In a typical preparative run, 31.7 g (0.47 mol) of **6** was treated at 0° with 25.5 g (0.235 mol) of *tert*-BuOCl added in small portions with continuous photoinitiation. After a negative starch–iodide test was achieved, solid sodium carbonate was added and the mixture distilled through an 18-in. Vigreux column at aspirator pressure without heating the pot above 25°. The distillate (21.1 g), collected in a cold trap, contained unreacted **6**, most of the *tert*-butyl alcohol, and some A (all statements concerning composition are based on glpc analysis unless indicated otherwise). The residue (32.5 g) was distilled very slowly through an annular Teflon spinning-band column and the following fractions were collected: (1) 3.4 g, bp <63° (11 mm); (2) 3.5 g, bp 63–65.5° (11 mm); (3) 5.0 g, bp 65° (11 mm); (4) 3.6 g, bp 65° (11 mm); (5) 0.7 g, bp 67–83° (10 mm); (6) 0.9 g, bp 83.5–85° (10 mm); and (7) 1.8 g, bp 86–100° (10 mm); a viscous residue remained. Fraction 1 contained largely *tert*-butyl alcohol and A. Fractions 2–4 were >98% pure B (30% isolated yield). Fraction 5 was a mixture of B and C. Fraction 6 was 75% C and 25% a new peak of similar retention time to C not initially present but formed during distillation. Fraction 7 was largely products of longer retention time than C. Attempts to distil more rapidly did not effect separation of B and C.

Product A was isolated by preparative glpc of the material remaining after washing fraction 1 with water; it was unstable on standing and gave erratic analytical data. The ir spectrum showed bands at 3280 (s), 2105 (w), 1680 (m), 1610 (m), 930 (s), and 918 (s) cm^{-1}; the nmr spectrum showed two broadened lines at δ 5.70 and 5.64 (area 2), a singlet at 4.07 (area 2), and a singlet at 1.78 ppm (area 1); A was thus assigned as 2-(chloromethyl)-1-buten-3-yne (**7**). Product B is assigned as *tert*-butyl 2-chloro-2-methyl-3-butyn-1-yl ether (**8**) on the basis of the ir and nmr spectra shown in Table XII.

Anal. Calcd for $C_9H_{15}ClO$: C, 61.88; H, 8.66; Cl, 20.30. Found: C, 61.98; H, 8.77; Cl, 20.13.

Product C, purified by preparative glpc of fraction 6, had the spectral properties shown in Table XIII and is assigned as *tert*-butyl 4-chloro-2-methyl-2,3-butadien-1-yl ether (**9**).

If distillation was carried out without added sodium carbonate, glpc monitoring of distillate and residue showed the gradual disappearance of B (**8**) and C (**9**) and their replacement by two new materials which were isolated by preparative glpc from distillation fractions. The first had infrared bands at 3550–3250 (broad), 3280 (s), and 2120 (w) cm^{-1}; the nmr spectrum consisted of four singlets at δ 3.72, 3.07, 2.67, and 1.82 ppm in the ratio of 2:1:1:3. It is assigned as 2-chloro-2-methyl-3-butyn-1-ol (**10**), an acid-catalyzed cleavage product of ether **8**. The second had infrared bands at 2820 (m), 2710 (w), 1685 (s), and 1640 (m) cm^{-1}, and nmr bands at δ 9.48 (s), 6.57 (broadened triplet, J = 7.5 Hz), 4.33 (d, J = 7.5 Hz), and 1.80 (broadened singlet) ppm in the ratio of 1:1:2:3. It is assigned as 4-chloro-2-methyl-2-butenal (**11**),[38] a rearranged acid-catalyzed cleavage product of **9**. The nmr chemical shift of the aldehydic singlet is suggestive of the (E) configuration.[21]

Acid-Catalyzed Cleavage of Ether 8. 2-Chloro-2-methyl-3-butyn-1-ol (10).—A solution of 3.45 g of ether **8** and 100 mg of *p*-toluenesulfonic acid monohydrate in 25 ml of benzene was refluxed for 2.5 hr at which point glpc analysis showed reaction to be complete. The solution was poured through a very short bed of Florisil which was eluted with 5 ml more of benzene. The benzene was distilled through a short Vigreux column; distillation through a short-path distillation head gave, after additional benzene, 1.65 g (71%) of product alcohol, bp 96–98° (100 mm) [lit.[39] bp 47° (10–12 mm)] which was essentially free from benzene and starting ether by glpc analysis (see spectral properties above).

Isomerization of Ether 8 to Ether 9.—A mixture of 5.17 g of **8**, 800 mg of freshly prepared cuprous chloride,[40] 625 mg of ammo-

(31) D. B. Denney and R. M. Hoyle, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, ORGN 41.

(32) W. H. Carothers and D. D. Coffman, *J. Amer. Chem. Soc.*, **54**, 4071 (1932).

(33) G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950).

(34) R. A. Jacobson and W. H. Carothers, *J. Amer. Chem. Soc.*, **55**, 1622 (1933).

(35) G. DeVries and H. G. Peer, *Recl. Trav. Chim. Pays-Bas*, **82**, 521 (1963).

(36) G. F. Hennion, C. C. Price, and T. F. McKeon, Jr., "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 683.

(37) J. L. H. Allan and M. C. Whiting, *J. Chem. Soc.*, 3314 (1953).

(38) H. Freyschlag, F. Stolp, W. Reif, and H. Pommer, German Patent 1,188,577 (March 1965); *Chem. Abstr.*, **62**, 13049 (1965).

(39) M. D. Mehta and D. Miller, British Patent 1,092,746 (to Beecham Group, Ltd.), (Nov 1967); *Chem. Abstr.*, **69**, 18593 (1968).

(40) R. N. Keller and H. D. Wycoff, *Inorg. Syn.*, **2**, 1 (1946).

TABLE XII

SPECTRAL PROPERTIES OF ADDUCTS tert-$\overset{a}{C_4H_9}O\overset{b}{C}HR_1\overset{c}{C}R_2ClC{\equiv}\overset{d}{C}R_3$

Adduct	R_1	R_2	R_3	Nmr bands, δ (ppm) H_a	H_b	H_c	H_d	Ir bands, cm^{-1} H—C≡	RC≡CR	RC≡CH	tert-C_4H_9–	COC
8	H	CH_3	H	1.23 (s)	3.50 (AB, J = 9.5)	[1.75 (s)][a]	2.47 (s)	3270		2120	1392, 1367, 1236, 1195	1092
14	H	H	CH_3	1.20 (s)	3.6 (m)	4.4 (m)	[1.87 (d, J = 2)][a]		2225		1396, 1369, 1237, 1200	1115
16	H	H	H	1.23 (s)	3.6 (m)	4.4 (m)	2.48 (d, J = 2.3)	3280		2125	1392, 1366, 1250, 1235, 1192	1105
24	CH_3	H	H	1.20 (s)	3.77 (m) [1.30 (d, J = 6)][a]	4.36 (d, d, J = 5, 2.5)	2.55 (d, J = 2.5)	3260		2120	1390, 1370, 1250, 1235, 1192	1082

[a] Values in brackets for CH_3 group at indicated hydrogen position.

TABLE XIII

SPECTRAL PROPERTIES OF ADDUCTS tert-$\overset{a}{C_4H_9}O\overset{b}{C}HR_1\overset{c}{C}R_2{=}C{=}\overset{d}{C}R_3Cl$

Adduct	R_1	R_2	R_3	Nmr bands, δ (ppm) H_a	H_b	H_c	H_d	Ir bands, cm^{-1} C=C=C	tert-C_4H_9–	COC
9	H	CH_3	H	1.20 (s)	3.92 (d, J = 2)	[1.82 (d, J = 2)][a]	5.98 (m)	1960	1390, 1364, 1234, 1192	1070
17	H	H	H	1.19 (s)	4.0 (broad d, J = 6)	5.67 (m)	6.08 (m)	1965	1392, 1369, 1235, 1195	1076
26[b]	CH_3	H	H	1.17 (s)	4.20 (5, J = 6.5) 4.17 (5, J = 6.5) [1.25 (d, $J \sim 6$)][a] [1.23 (d, $J \sim 6$)][a]	5.52 (m)	6.00 (d, d, J = 5.7, 1.6) 5.96 (d, d, J = 5.7, 1.5)	1960	1390, 1370, 1256, 1230, 1197	1097

[a] Values in brackets for CH_3 group at indicated hydrogen position. [b] Two sets of values for two diastereomers.

nium chloride, 2.0 ml of water, and 0.65 ml of concentrated hydrochloric acid was stirred magnetically in a stoppered flask.[22] Occasional glpc analysis of the upper layer showed the ratio of 9:8 to be ~1:1 after 24 hr, ~4:1 after 48 hr, and >10:1 after 110 hr at which point the mixture was flooded with water. Organic material was collected by extraction with pentane but considerable insoluble tarry residue was discarded. After drying and evaporation of the pentane, distillation through a short Vigreux column gave, after a small forerun, (1) 1.5 ml, bp 88–92° (15 mm), and (2) 0.3 ml, bp 92° (15 mm). Glpc analysis showed 1 to be >80% the allenic isomer and 2 to be > 95% pure.

Control Experiments for Reaction of 2-Methyl-1-buten-3-yne (6) with *tert*-BuOCl. A. Telomer Formation.—Glpc analyses were carried out on selected runs on column "O" at 160° to search for possible telomers. At a 10:1 ratio of 6:*tert*-BuOCl, some extra peaks were observed at retention times longer than those of the monoadducts (<5% of 8). However, these could not be detected at a 40:1 ratio of reactants and increased significantly at a 1.5:1 ratio of reactants. Thus the less volatile products seem to be the result of secondary reactions of primary products rather than telomers.

B. Reactivity of Major Adduct 8.—A mixture of 5.24 mmol of enyne 6, 4.10 mmol of 8, 3.66 mmol of chlorobenzene (internal standard), and 3.96 mmol of *tert*-BuOCl was illuminated until reaction was complete. Glpc analysis showed, in comparison to chlorobenzene, 1.72 mmol of 6 and 5.00 mmol of 8 remaining. Thus 3.52 mmol of 6 was consumed. If we assume that the remaining 0.42 mmol of *tert*-BuOCl reacted entirely with 8, then 1.32 mmol of 8 must have been formed from 6. This yield of 1.32/3.52 × 100% = 38% is as expected (see Table I). From these data one can then calculate that 6 is at least eight times as reactive as 8 toward *tert*-BuOCl.

C. Reactivity of Minor Adduct 9.—In similar fashion a mixture of 4.07 mmol of 6, 3.01 mmol of 9, 3.05 mmol of chlorobenzene, and 2.95 mmol of *tert*-BuOCl reacted to leave 2.72 mmol of 6 and 1.83 mmol of 9. To a first approximation then 1.35 mmol of *tert*-BuOCl reacted with 6 and the remaining 1.60 mmol reacted with 9; a 31% yield of 9 from 6 would be calculated. Thus adduct 9 is slightly more reactive than starting material 6 toward *tert*-BuOCl but not by a margin of more than about twofold.

Product Identification from Reaction of 1-Penten-3-yne (12) and *tert*-BuOCl.—Small-scale reactions with large excesses of 12 showed two products, D and E, other than *tert*-BuOH, by glpc analysis. Reaction of 9.0 g of 12 and 7.4 g of *tert*-BuOCl at ~0° gave on direct distillation from sodium carbonate after reaction: (1) forerun, bp <40° (15 mm); (2) 0.37 g, bp ~40° (15 mm); and (3) 4.6 g, bp 48–50° (1.5 mm). Fraction 2, 95% D by glpc analysis, had ir bands at 2240 (w), 1615 (m), 975 (s), and 930 (s) cm^{-1} and nmr bands at δ 5.9–5.3 (m) and 4.23 (d, $J \sim 1$ Hz) ppm in the ratio of 3:2. It was assigned the structure 5-chloro-1-penten-3-yne (13) [lit.[41] bp 60° (65 mm)]. Fraction 3, >95% E with residual D, had the spectral properties shown in Table XII and was assigned the structure *tert*-butyl 2-chloro-3-pentyn-1-yl ether (14).

Anal. Calcd for $C_9H_{15}ClO$: C, 61.88; H, 8.66; Cl, 20.30; O, 9.16. Found: C, 61.63; H, 8.52; Cl, 20.60; O, 9.40.

Attempted Isomerization of Ether 14 to Its Allenic Isomer.—A mixture of 1.212 g of 14, 147 mg of ammonium chloride, 191 mg of freshly prepared cuprous chloride,[40] 0.47 ml of water, and 0.15 ml of concentrated hydrochloric acid was stirred at room temperature in a stoppered flask for 72 hr. The mixture was partitioned between water and pentane. Glpc analysis of the pentane extract showed the starting material with <5% of a new band of slightly shorter retention time. Ir analysis of the residue after evaporation of the pentane confirmed that the starting material had been recovered.

Product Identification from Reaction of Vinylacetylene (15) and *tert*-BuOCl.—Vinylacetylene was passed into the reaction vessel as a gas under nitrogen and condensed by means of a Dry Ice condenser. Low conversion runs carried out in an ice bath with or without added 1,1,2-trichlorotrifluoroethane solvent showed *tert*-BuOH and four other products, F–I, by glpc analysis. In preparative runs at higher *tert*-BuOCl concentration carried to 50% conversion, however, product G was no longer observed and the amount of product I was larger compared to F and H. Product F was isolated in 25% yield as a pure fraction, bp 52° (6 mm), $n^{22}D$ 1.4422, by distillation and had spectral properties shown in

(41) L. Crombie, S. H. Harper, F. C. Newman, D. Thompson, and R. J. D. Smith, *J. Chem. Soc.*, 126 (1956).

Table XII. It is assigned as *tert*-butyl 2-chloro-3-butyn-1-yl ether (16).

Anal. Calcd for $C_8H_{13}ClO$: C, 59.81; H, 8.16; Cl, 22.07; O, 9.96. Found: C, 59.85; H, 8.06; Cl, 22.06; O, 10.10.

Products H and I could not be obtained pure by distillation but only as mixtures with F; preparative glpc gave pure samples. Product H was assigned as *tert*-butyl 4-chloro-2,3-butadien-1-yl ether (17) in the basis of the spectral properties shown in Table XIII. Product I was identical with an authentic sample of 2,4-dichloro-2-butenal (18) prepared from aldol condensation of chloroacetaldehyde:[23] ir 2820 (m), 2725 (w), 1700 (s), and 1625 (m) cm^{-1}; nmr δ 9.47 (s), 7.03 (t, J = 7 Hz), and 4.44 (d, J = 7 Hz) ppm.

All attempts to isolate the transient product G by preparative glpc of residues from low-conversion runs failed. However, a hydrolysis product was obtained as follows: A mixture of 25 ml of vinylacetylene and 20 ml of 1,1,2-trichlorotrifluoroethane was treated at reflux under a Dry Ice condenser (internal temperature ~18°) with 3 ml of *tert*-BuOCl added in small portions with continuous illumination. After reaction was complete, the Dry Ice condenser was replaced with a water-cooled condenser and a stream of nitrogen was used to drive the excess vinylacetylene into a second reaction vessel topped by the Dry Ice condenser. This was treated with 15 ml more of solvent and reacted with 2.5 ml of *tert*-BuOCl. A second repetition was carried out with 15 ml more of solvent and 1.5 ml of *tert*-BuOCl. The three combined residues were then evaporated at room temperature and aspirator pressure to remove solvent. The resulting crude product, which by glpc analysis contained F–I in amounts characteristic of low-conversion runs, was then stirred with a mixture of 8 ml of methanol and 4 ml of concentrated hydrochloric acid for 40 min at room temperature. The mixture was flooded with water and extracted with pentane. The pentane extracts were washed with dilute sodium bicarbonate solution and dried over calcium chloride. Glpc analysis showed that F and H had survived, G and I had disappeared, and two new bands had appeared, one of retention time shorter than F and the other of retention time longer than I. The pentane was distilled and the residue evaporated at 25° down to 50 mm. A distillate was then trapped by gradually lowering the pressure to 1 mm and raising the pot temperature to 40°. Preparative glpc of this material gave the more volatile new product in 85% purity whose ir and nmr spectral properties coincided with those of 2-chloro-2-butenal (20)[42] and which gave a DNP derivative, mp 225–226° dec (lit.[42] mp 229 dec). On the basis of this hydrolysis product and of dichloroaldehyde 18, product G is assigned as *tert*-butyl 2-chloro-1,3-butadien-1-yl ether (19).

Product Identification from Reaction of *cis*-3-Penten-1-yne (21) and *tert*-BuOCl.—Low-conversion runs showed *tert*-BuOH and seven distinct products, J–P, by glpc analysis, but product P disappeared in preparative runs. Treatment of 11.1 g of 21 with 9.1 g of *tert*-BuOCl in the usual fashion and direct distillation of the reaction mixture (added sodium carbonate) through a spinning-band column gave, after a forerun containing excess 21 and *tert*-BuOH, the following fractions: (1) 0.48 g, bp 30–35° (120 mm), largely 21 and *tert*-BuOH; (2) 0.88 g, bp <30° (25 mm), largely products J and K; (3) 0.13 g, bp <30° (20 mm), J and K; (4) 0.10 g, bp 25–40° (3 mm); (5) 1.55 g, bp 40–41° (2 mm), largely products L–N; (6) 0.70 g, bp 50–60° (2 mm), largely products M–O; and (7) 1.75 g, bp 60–80° (2 mm), product O plus less volatile materials formed during distillation. Preparative glpc on fractions 2 and 3 gave >90% pure samples of J and K. Product J had ir bands at 3300 (s) and 1615 (w) cm^{-1} but none in the 1000–925-cm^{-1} region; the nmr spectrum showed a multiplet at δ 5.88 which could be analyzed as an AB pattern (J_{AB} = 10.6 Hz) with the lower field lines further split into triplets (J = 7.2 Hz) and the upper field lines further split into doublets (J = 2.2 Hz), a doublet at 4.27 (J ~ 7 Hz), and a doublet at 3.20 (J ~ 2 Hz) ppm with relative areas of 2:2:1. Product K had ir bands at 3295 (s), 1630 (w), and 955 (vs) cm^{-1}; the nmr spectrum showed an AB pattern (J_{AB} = 16.7 Hz) at δ 6.03 with the lower field lines further split into triplets (J = 6.5 Hz) and the upper field lines slightly broadened, a doublet at 4.05 (J = 6.5 Hz) and a doublet at 2.88 (J ~ 2 Hz) ppm with relative areas of 2:2:1. These spectra are fully consistent with the structures *cis*-5-chloro-3-penten-1-yne (22) for J and the trans isomer (23) for K.[24] From fraction 5 it was possible to collect product L, a mixture of L and M, and product N. Spectral properties of L are shown in Table XII; these allow the skeletal assignment *tert*-butyl 3-chloro-4-pentyn-2-yl ether; the stereochemical assignment as threo (24) is described below. The nmr spectrum of the mixture of L and M was identical with that of L alone except for appearance of two doublets for the C≡C—H protons separated by 1 Hz, and hence M is assigned as the erythro isomer 25. Product N was homogeneous on all glpc columns tried but the nmr spectrum at 100 MHz (Table XIII) clearly showed the presence of the two diastereomeric modifications of *tert*-butyl 5-chloro-3,4-pentadien-2-yl ether (26) in comparable amounts. Product O was collected from fraction 6 and showed ir bands at 2835 (m), 2725 (w), 1700 (s), and 1625 (m) cm^{-1}, and nmr bands at δ 9.43 (s), 6.98 (d, J = 9 Hz), 5.10 (m), and 1.73 (d, J = 6.5 Hz) ppm with relative areas of 1:1:1:3; this product is therefore assigned as 2,4-dichloro-2-pentenal (27). No success was achieved in isolating product P but, by analogy to the results for vinylacetylene, it is tentatively assigned as *tert*-butyl 2-chloro-1,3-pentadien-1-yl ether (28), probably with a cis 3,4 double bond.

Product Identification from Reaction of *trans*-3-Penten-1-yne (29) and *tert*-BuOCl.—Low conversion runs showed *tert*-BuOH, products J–O (22–27), a new transient Q, but no P. To confirm the glpc assignments, preparative glpc was again used to isolate 22, 23, a mixture of 24 and 25, 26, and 27; spectral properties were in full agreement with those of the products derived from the cis starting material 21. Q is tentatively assigned as a second geometrical isomer of 28 (probably trans-3,4).

Hydrogenation of *threo-tert*-Butyl 3-Chloro-4-pentyn-2-yl Ether (24).—A solution of 24 (120 µl, 90% pure) in 2 ml of ethyl acetate was hydrogenated for 24 hr at 1 atm over rhodium on carbon catalyst but no hydrogen uptake occurred. Addition of palladium on charcoal catalyst at this point did lead to consumption of 30 ml of hydrogen (STP) in 2 hr. The major product was collected by glpc and shown to be identical with *threo-tert*-butyl 3-chloro-2-pentyl ether.[25]

Quantitative Results.—The results shown in Tables I–IV and VI–VIII were obtained by mixing the appropriate quantities of reagents (enyne, *tert*-BuOCl, and cyclohexane when used in competitive runs) (total volume usually 10 ml) in a small flask under a reflux condenser, flushing briefly with nitrogen, and then illuminating with a 275-W sun lamp under nitrogen until a negative starch–iodide test was obtained (30 min–3 hr). Glpc analysis was then carried out directly on the total mixture after addition of a known amount of chlorobenzene or benzonitrile as an internal standard for calculation of yields. Results at 25° were carried out in a constant temperature bath, those at 0° in an ice bath, and those at −75° in a Dry Ice bath. For vinylacetylene (Table V), a Dry Ice reflux condenser was used, the vinylacetylene was condensed into the flask, and the 1,1,2-trichlorotrifluoroethane and *tert*-BuOCl were then added. The temperature (18–20°) was that maintained in the refluxing mixture. Glpc samples were introduced with a cooled syringe.

Registry No.—*tert*-Butyl hypochlorite, 507-40-4; 6, 78-80-8; 7, 26409-04-1; 8, 26394-22-9; 9, 26394-23-0; 10, 20116-17-0; 11, 26394-25-2; 12, 646-05-9; 14, 26394-27-4; 15, 689-97-4; 16, 26394-29-6; 17, 26394-30-9, 18, 26394-31-0; 21, 1574-40-9; 22, 21613-38-7; 23, 21613-37-6; 24, 26394-35-4; 26, 26394-36-5; 27, 26394-37-6; 29, 2004-69-5.

(42) L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1966).