

Positive Halogen Compounds. XI. "Spontaneous" Chain Initiation and the Reaction of *t*-Butyl Hypohalites with Acetylenes¹

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The radical chain halogenation of styrene and 2-butyne by *t*-butyl hypochlorite or hypobromite occurs spontaneously in the dark on mixing, yielding, in the latter case, 1-halo-2-butyne as the major product and inducing halogenation of other hydrocarbons. Slower spontaneous initiation occurs with several 1-phenylalkynes. It is suggested that initiation involves the concerted breaking of the O-X bond of the hypohalite and addition of X to the π -electron system of the unsaturated molecule. In support of this, small yields of halogen addition products (styrene dihalide and dihaloethylenes) are isolated from the reactions. *t*-Butoxy radicals readily attack acetylenes to give good yields of propargylic halides with little tendency to add to the triple bond. Competitive experiments show that acetylenes and the corresponding olefins have quite similar reactivities.

In the course of a survey of the reaction of *t*-butyl hypochlorite with a variety of hydrocarbons,² an unusually rapid reaction was noted with styrene. Although the products and the retarding effect of oxygen were both consistent with a radical chain, the reaction was remarkable in that no irradiation or added radical initiator was required. Similar "spontaneous" reactions have now been observed with substituted acetylenes,³ and this paper describes a study of the products and conditions of these processes, together with a survey of the relative reactivities of a number of acetylenes and olefins toward *t*-butyl hypochlorite and the *t*-butoxy radical.

Reaction with Styrene. Styrene reacts spontaneously and exothermically with *t*-butyl hypochlorite or hypobromite in total darkness at 0–5°. The reaction is extremely vigorous, but may be controlled by slow addition of hypohalite to degassed solutions of styrene under nitrogen with cooling of the reaction mixture after each addition. The radical nature of this dark reaction is evidenced by its inhibition by oxygen or *t*-butyl catechol, by the formation of the anti-Markovnikov product, 2-chloro-2-phenylethyl *t*-butyl ether, and by the induced chlorination of cyclohexane. The dark reaction of equimolecular quantities of hypochlorite, styrene, and cyclohexane gave a relative

reactivity cyclohexane–styrene = 1.14, which agrees reasonably with the light-initiated value² of 1.74 at 40° but may include some polar addition. Products of dark reactions are compared with those of experiments carried out under strong illumination in Table I.

Table I. Reaction of *t*-Butyl Hypochlorite with Styrene^a

Run no.	1,2	3,4 ^b	5	6	7	8	9 ^c
CCl ₄ ^d	0	0	0	2	4	4	0
D (dark) or L (light)	D	D	L	D	D	L	D
Products	% yields						
(CH ₃) ₂ CO	5.7	17.1	4.9	3.2	4.3	4.1	0.3
	6.6	9.9	3.5				0.5
(CH ₃) ₃ COH	13.6	22.5	10.5	11.9	15.4	13.9	11.8
	14.3	17.8	12.6				16.7
C ₆ H ₅ CHClCH ₂ -OC(CH ₃) ₃ ^e	68.8	25.5	63.6	62.5	65.6	59.3	67.2
Total C ₄ H ₈ O	88.1	65.1	79.1	77.7	85.3	77.3	79.2
	89.7	59.6	78.5				89.5
C ₆ H ₅ CHCl-CH ₂ Cl	2.3	3.9	1.3	8.0 ^f	7.2 ^f	5.9 ^f	...
Gas ^g	0	3.3	0.3	1.4	1.0	0	...
			1.3				

^a 1:1.5 mole ratios unless indicated at 0–5°. ^b Styrene added to hypochlorite, ^c *t*-Butyl hypobromite, 1:2.2 mole ratio, addition product analyzed by n.m.r. (see Experimental). ^d Moles/mole of hypochlorite. ^e Determined as C₆H₅CH₂CH₂OC(CH₃)₃ after hydrogenation. ^f Determined as ethylbenzene after hydrogenation. Runs 1–5 gave 6–18% by this technique. ^g Volatile products not condensed by Dry Ice.

With the exception of runs 3 and 4 where styrene was added to *t*-butyl hypochlorite, and in which (as might be anticipated) relatively large amounts of side reactions occur, results are quite consistent and product yields appear largely independent of irradiation and the presence of CCl₄ solvent. Analyses in general were carried out by gas-liquid chromatography (g.l.c.). The major product, 2-chloro-2-phenylethyl *t*-butyl ether, was not determined directly but as 2-phenylethyl *t*-butyl ether after hydrogenation, so that the analysis may include small amounts of more highly chlorinated products. In any case, however, identification of this ether provides further confirmation of the direction of addition of *t*-butyl hypochlorite to styrene, previously deduced from elemental analysis and easy reaction with AgNO₃.² In the *t*-butyl hypobromite experiment, run 9, the corresponding bromoether was further identified by its n.m.r. spectra. 1,2-Dichlorophenylethane was

(1) Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

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

(3) Preliminary deductions as to the existence of a "spontaneous" reaction were based upon the detonation of sealed tubes containing *t*-butyl hypochlorite and 2-butyne on warming from a liquid N₂ bath.

Table II. Reaction of *t*-Butyl Hypochlorite with 2-Butyne^a

Run no. C ₄ H ₈ :ROCl:CCl ₄ D (dark) or L (light) Products	1 4:1:0		2 L		3 D		4 3.2:1:4.1 L		5 ^b D		6 ^b 3.2:1.0:4.4 L		
	%												
(CH ₃) ₂ CO	3.4	8.4	6.2 ± 0.5 ^c	5.7 ± 0.9	3.7 ± 0.8	3.5 ± 1.4	86.8	82.5	93.8 ± 1.8	94.2 ± 3.9	74.7 ± 5.8	77.3 ± 5.4	
(CH ₃) ₃ COH	90.2	90.9	100 ± 1.3	99.8 ± 4.7	78.4 ± 5.0	80.7 ± 4.1	41.4	47.8	38.2 ± 1.0	40.7 ± 1.7	24.0 ± 5.5	28.2 ± 2.0	
Total C ₄ H ₈ O-	6.3	8.4	9.3 ± 0.2	9.2 ± 1.7	16.5 ± 2.4	17.4 ± 0.9	CH ₃ C≡CCH ₂ Cl	2.5	3.3	3.6 ± 0.2	3.4 ± 0.3	...	
CH ₃ CCl=CClCH ₃	64.0	77.8	71.2 ± 0.2	72.4 ± 2.7	CH ₃ CCl=CClCH ₃	6.3	8.4	9.3 ± 0.2	9.2 ± 1.7	16.5 ± 2.4	17.4 ± 0.9
Product X ^d	Product X ^d	2.5	3.3	3.6 ± 0.2	3.4 ± 0.3
Total Cl	Total Cl	64.0	77.8	71.2 ± 0.2	72.4 ± 2.7

^a At room temperature. ^b *t*-Butyl hypobromite, products are the corresponding bromides. ^c Experimental errors in all tables are average deviations of duplicate or triplicate experiments. ^d Assumed dimer.

determined directly by g.l.c. and as ethylbenzene after hydrogenation. As indicated in Table I, the latter method gave higher values which could arise from hydrogenolysis of a polar addition product or through reduction of dichlorophenylethane which had undergone further chlorination. The appreciable yields (10–15%) of *t*-butyl alcohol indicate that such substitution reactions must indeed be occurring. Significant amounts of acetone formation at this low temperature also show that styrene, like other aromatics, falls in the group of solvents which favor the unimolecular scission of *t*-butoxy radicals to acetone and methyl radicals over its bimolecular reactions with substrates.⁴ For reasons which are not evident, however, acetone yields are lower for reactions employing *t*-butyl hypobromite.

Reaction with 2-Butyne. *t*-Butyl hypochlorite underwent a violent exothermic reaction with 2-butyne in the dark at room temperature to yield the radical substitution product 1-chloro-2-butyne, *trans*-1,2-dichloro-2-butene, and other products. The reaction again could be controlled by slow addition and further by dilution with CCl₄. Although in dilute solution strongly illuminated systems appear to react even more rapidly, no significant change in products was noted. Results of several runs are listed in Table II, in which experimental errors represent the spread of duplicate experiments. In every case 1-halo-2-butyne was the major product, and the quantitative yield of acetone and *t*-butyl alcohol in runs 3 and 4 indicates that essentially no addition to the acetylenic triple bond takes place. On the other hand, halogen balances were low and it was found that in all experiments 1.1–1.2 moles of acetylene was consumed per mole of hypochlorite employed. Apparently these observations are accounted for by the formation of higher boiling products. Of these, one (product X) was partially characterized as a dimer containing four chlorine atoms, discussed further in the Experimental part of this paper. Runs 5 and 6 employed *t*-butyl hypobromite. Here reaction was, if anything, more rapid. Products were qualitatively similar, although yields of 1-bromo-2-butyne were reduced, more 2,3-dibromo-2-butene is formed, and material balances were poorer.

Further evidence for the radical nature of the hypochlorite-2-butyne reaction was obtained by demonstrating the induced chlorination of toluene to benzyl chloride (Table III). Material balances are comparable

with those in Table II and dark and light reactions again give the same result. As might be expected, yields of 1-chloro-2-butyne are reduced since chain-carrying radicals are diverted to attack on toluene. On the other hand there is little change in the yield of 2,3-dichloro-2-butene. Relative reactivities calculated from experiments such as these are discussed further below.

Table III. Reaction of *t*-Butyl Hypochlorite with 2-Butyne in the Presence of Toluene^a

Products	— % Yield based on ROCl. % —	
	Dark	Light
(CH ₃) ₂ CO	5.2 ± 0.2	5.9 ± 0.3
(CH ₃) ₃ COH	93.8 ± 0.3	96.6 ± 2.9
Total C ₄ H ₈ O	99.0 ± 0.2	102.5 ± 2.5
CH ₃ C≡CCH ₂ Cl	24.6 ± 0.2	26.8 ± 1.1
CH ₃ CCl=CClCH ₃	6.7 ± 0.5	6.7 ± 0.2
C ₆ H ₅ CH ₂ Cl	17.5 ± 0.7	18.4 ± 1.3
Product X	2.8 ± 0.2	3.2 ± 0.1
Total Cl	66.7 ± 0.3	71.4 ± 0.6

^a Room temperature, [C₄H₈]:[C₆H₅CH₃]:[ROCl]:[CCl₄] = 1.9:1.9:1.0:2.9.

Reactions with Other Acetylenes. We have also made a briefer investigation of the reaction of *t*-butyl hypochlorite with three other acetylenes: 3-methyl-1-phenyl-1-butyne, 1-phenyl-1-butyne, and 1-phenylpropyne. The reaction with 3-methyl-1-phenyl-1-butyne was found to occur spontaneously at room temperature (25–30°) but considerably more slowly than in the case of styrene or 2-butyne. In CCl₄ irradiated experiments were complete in 24 hr., those in the dark in 48. Results of experiments are listed in Table IV where it will be seen that again the major product arises from attack on propargylic hydrogen, some dichloroolefin is produced, and little if any addition of *t*-butoxy radical to the triple bond occurs, since almost all *t*-butoxy radicals are accounted for as *t*-butyl alcohol and acetone. Light and dark reactions give similar results, but in this case less than 1 mole of acetylene is consumed per mole of hypochlorite, suggesting that further chlorination of intermediate products (rather than polymer formation) is the chief side reaction.

1-Phenyl-1-butyne reacts more slowly with *t*-butyl hypochlorite, the light reaction requiring 3 days in CCl₄ and the dark reaction 4–5 days. 1-Phenylpropyne in turn is slower still, requiring 4–5 days for irradiated reactions and over 2 weeks for those in the

(4) C. Walling and P. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

Table IV. Reaction of *t*-Butyl Hypochlorite with 3-Methyl-1-phenyl-1-butyne^a

[C ₁₁ H ₁₂]:[ROCl]:[CCl ₄] D (dark) or L (light) Products	1.1:1.0:2.1		1.5:1.0:0	
	D	L	D ^b	L ^c
(CH ₃) ₂ CO	4.5 ± 1.0	5.8 ± 0.7	4.9	26.6
(CH ₃) ₃ COH	93.2 ± 1.1	91.7 ± 3.2	93	68.9
C ₄ H ₈ O balance	97.7 ± 2.1	97.5 ± 2.5	97.9	95.5
C ₆ H ₅ ≡CC(CH ₃) ₂ Cl	36.8 ± 2.3	46.8 ± 5.1	45.6	44.3
C ₆ H ₅ CCl=CClCH(CH ₃) ₂				
<i>trans</i>	12.0 ± 2.5	10.1 ± 3.2	12.2	7.4
<i>cis</i>	3.0 ± 0.7	2.6 ± 1.1	4.0	4.9
Cl balance	68.8 ± 4.5	74.0 ± 2.1	78.0	68.9
C ₁₁ H ₁₂ -ROCl used, %	82 ± 2	75 ± 5	69	59

^a At 25–30°. ^b Single experiment. ^c Single experiment accidentally contaminated with water which might account for high acetone yield (?).

dark. Products are listed in Tables V and VI, and again show predominant attack on propargylic hydrogen, little if any addition, the formation of appreciable amounts of dichloroolefin, and no significant difference between light and dark reactions.

Table V. Reaction of *t*-Butyl Hypochlorite with 1-Phenyl-1-butyne^a

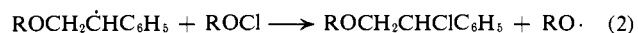
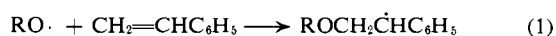
Products	Yield, %	
	Dark (2)	Light (2)
(CH ₃) ₂ CO	3.4 ± 0.4	4.1 ± 0.1
(CH ₃) ₃ COH	98.4 ± 3.1	99.2 ± 3.5
C ₄ H ₈ O balance	101.8 ± 3.5	103.3 ± 3.4
C ₆ H ₅ C≡CCHClCH ₃	38.8 ± 6.3	41.3 ± 2.6
C ₆ H ₅ CCl=CClCH ₂ CH ₃ ^b	3.0 ± 0.4	1.8 ± 0.7
C ₁₀ H ₁₀ balance	66 ± 8	63 ± 2
C ₁₀ H ₁₀ accounted for	66 ± 18	68.6 ± 1.3

^a [C₁₀H₁₀]:[ROCl]:[CCl₄] = 1.4:1.0:2.6. ^b The *trans* isomer; some *cis* formed but not determined quantitatively.

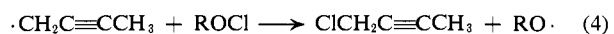
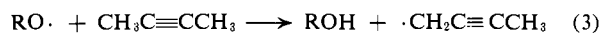
Table VI. Reaction of *t*-Butyl Hypochlorite with 1-Phenylpropyne

Products	Yield, %	
	Dark (2)	Light (3)
(CH ₃) ₂ CO	5.8 ± 0.1	5.2 ± 0.7
(CH ₃) ₃ COH	97.1 ± 6.8	96.4 ± 1.3
C ₄ H ₈ O balance	102.9 ± 6.8	101.6 ± 2.0
C ₆ H ₅ ≡CCH ₂ Cl	25.8 ± 1.2	21.2 ± 2.3
C ₆ H ₅ CCl=CClCH ₃		
<i>trans</i>	2.9 ± 0.1	4.2 ± 1.2
<i>cis</i>	1.3 ± 0.1	2.0 ± 1.4
C ₉ H ₈ -ROCl used	43 ± 9	55 ± 5
C ₉ H ₈ balance	72.8 ± 17.4	50.4 ± 3.4

The Nature of the "Spontaneous" Initiation Process. The experiments just described show clearly that irradiation has little effect on the rates or products of reaction of *t*-butyl hypochlorite with styrene or a number of substituted acetylenes. The major products of the dark reactions are those anticipated from radical chain halogenation with styrene *via* radical addition (eq. 1 and 2, where R = *t*-C₄H₉) and with the acetylenes

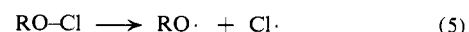


via attack on propargylic hydrogen (eq. 3 and 4).



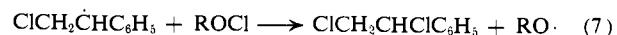
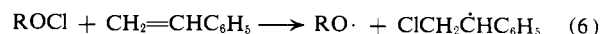
As we have seen, the radical chain nature of the

reactions is further supported by their retardation by oxygen or *t*-butylcatechol and the induced chlorination of cyclohexane and toluene. We must accordingly ask what is the nature of the initiating process. Two possibilities can be quite conclusively eliminated. The simple homolytic cleavage of *t*-butyl hypochlorite



is implausible since similar dark reactions do not occur in the presence of other easily chlorinated substrates.⁵ Further, since *D*(HO-Cl) and *D*(HO-Br) are reported as 60 and 56 kcal./mole compared with *D*(HO-OH) of 52 kcal.,⁶ by plausible analogy *D*(RO-Cl) and *D*(RO-Br) should both be expected to be higher than *D*(RO-OH) which is at least 40 kcal.⁷ Second, initiation by adventitious impurities seems unlikely. The very high rates of reaction with styrene and 2-butyne would require large amounts of initiator (our styrene samples showed no tendency to polymerize rapidly on standing). Large amounts would also be required with the phenylacetylene derivatives since strong light produced only a small increase in rate.

The remaining alternative is some sort of "poly-molecular" radical forming reaction between styrene or acetylene and hypochlorite. We believe that the formation of 1,2-dichlorophenylethane from styrene and the various dichloroethylenes from the acetylenes is a measure of the extent of this reaction and an indication of the process involved, which we suggest rather schematically as eq. 6 and 7.



Before looking further into the nature and plausibility of the actual radical forming process (eq. 6) we observe that the appreciable yields of dichlorides indicate that kinetic chains must be very short (6–50) in our experiments. This is certainly consistent with our results since the very fast reactions with styrene and 2-butyne point to remarkably high radical concentrations, and the insensitivity of the phenylacetylene derivatives to photoinitiation indicate short kinetic chains.⁸ It should be noted that dichlorides should

(5) For comparison, cyclohexane solutions of *t*-butyl hypochlorite are stable for days in the dark, but react in a few minutes at light intensities such as we have employed here. Simple olefins show similar behavior, and *t*-butyl hypobromite-cyclohexane mixtures are also stable.

(6) T. L. Cottrell "The Strengths of Chemical Bonds," Academic Press Inc., New York, N. Y., 1954.

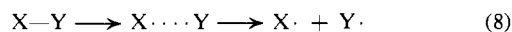
(7) S. W. Benson, *J. Chem. Phys.*, **40**, 1007 (1964).

(8) We have no present explanation of this fact, but rates of photo-halogenation with *t*-butyl hypochlorite vary greatly with substrate, and

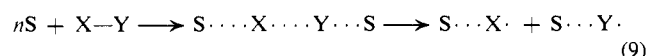
also be products of ordinary photoinitiation of olefin halogenation by hypochlorite, *via* chlorine addition followed by eq. 7. However, in "normal" long-chain processes only traces of dichloride would be produced, and indeed none was ever noted in our earlier study of the halogenation of simple alkenes.²

If reaction 6 actually represents the process of radical formation, it probably belongs to the class of radical processes which are greatly influenced by interactions between electronegative radicals and loosely held (π and unshared pair) electron systems, the importance of which is being increasingly evident. In one type of example, solvent effects on the reactions of radicals such as chlorine atoms⁹ or alkoxy radicals⁴ appear to involve some interaction of this sort. In another, cases of the effect of surrounding molecules on the ease of homolytic bond scissions are accumulating rapidly. As illustrations, olefins initiate an almost instantaneous production of radicals from molecular fluorine, even at very low temperature,¹⁰ and a similar reaction between molecular chlorine and cyclohexene has recently been elegantly demonstrated by Poutsma.¹¹ In the peroxide series, examples include the bimolecular radical forming reaction between dimethoxy-stilbene and negatively substituted benzoyl peroxides¹² and the accelerated homolysis of hydroperoxides in olefinic media.¹³ The most striking cases are those in which the dissociating species provides its own interacting functional group, a process which Martin has termed "anchimeric acceleration of homolysis" and provided examples, *e.g.*, the decomposition of *t*-butyl (*o*-thiophenyl)perbenzoate.¹⁴ The relation between these two sorts of processes becomes evident when we realize that solvent effects on the reactions of radicals involve interactions between solvent and radicals and between solvent and transition states of the radicals as they react.¹⁵ Referring to such interactions loosely as "solvation," it is easy to see how, if transition states for the reaction of already formed radicals show evidence for extensive solvation, similar solvation is also possible for the transition state of a radical-forming process involving homolysis of a weak bond.

If the simple homolysis is represented as eq. 8 the



solvated process might be written as eq. 9 with relative



energetics shown schematically in Figure 1, path A representing reaction 8 and B reaction 9. If $D(X-Y)$ is large and at least one of the fragments can react rapidly with S, a still lower energy path may be available for the dissociation, with a transition state on the

we are engaged in kinetic studies which we hope will provide a rational interpretation.

(9) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958), and subsequent papers.

(10) W. T. Miller, Jr., S. D. Koch, Jr., and F. W. McLafferty, *ibid.*, **78**, 4992 (1956).

(11) M. L. Poutsma, *ibid.*, **85**, 3510 (1963).

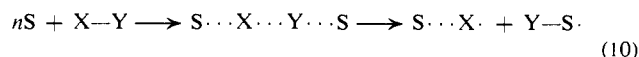
(12) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961).

(13) C. Walling and L. Heaton, *ibid.*, **87**, 38 (1965).

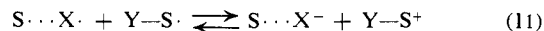
(14) W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962).

(15) To date, solvent effects have been observed chiefly through changes in relative rates of competing reactions. Here it is important to keep in mind that the observed effects arise solely from interactions between transition states and solvent, resulting in changes in their relative energy: *cf.* C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963).

way to forming a covalent bond to S indicated by path



C in Figure 1. Presumably eq. 9 and 10 could be distinguished by radical trapping and identification, providing reaction of the initial radicals in eq. 9 with solvent is not too rapid, or they might be predicted from a knowledge of bond dissociation and radical solvation energies. In the case that the charge transfer equilibrium lies to the right path C may be generalized



and passes smoothly to an S_N2 displacement with no real change of mechanism. As examples of this shift, the reaction of benzoyl peroxide with tertiary amines gives only low yields of radicals,¹⁶ while reaction with phenols is usually an entirely nonradical process.¹⁷

On the basis of energetics, path C, concerted bond formation, would seem to be required for rapid radical-forming processes for halogens, and also for the hypohalite reactions described here. Assuming a minimum value of $D(RO-Cl)$ of 40 kcal. (see above), over 20 kcal. of solvation energy would be required for homolysis by path C to account for the high rates observed. On the other hand, it has been estimated that 49 kcal. of energy is liberated by addition of a chlorine atom to styrene,¹⁸ so coupling this process with cleavage of the $RO-Cl$ bond could here make the over-all process actually exothermic. Within this general framework there seem to be wide differences in types of solvent-assisted homolysis, and little close parallel between molecules which lead to radical formation from peroxides, hypohalites, and halogens.¹⁹ Further, spontaneous radical formation also appears to take place on addition of hypochlorite to some aldehydes and ethers.²⁰ Although their exact nature remains mysterious, the generality and unexplained distribution of such processes suggest caution in the use of hypohalites as halogenating reagents in unexplored systems.

Relative Reactivities of Acetylenes. In addition to our observations on radical-forming processes, our results on *t*-butyl hypochlorite-acetylene systems show that the reaction may have synthetic utility as a technique for preparing propargylic chlorides since the products are essentially free of chloroallenes and yields could presumably be raised by using higher acetylene: hypochlorite ratios. In order to demonstrate the specificity of attack we have compared relative reactivities of a series of acetylenes with the corresponding olefins by our usual technique of chlorinating mixtures and determining ratios of unreacted starting material.² Results, listed in Table VII, are somewhat qualitative since we did not make a detailed examination of products, and also because of possible effects of changing media.⁴

We find that 2-butyne is somewhat less reactive than 2-butene, which parallels the observation that bond

(16) C. Walling and N. Indictor, *ibid.*, **80**, 5814 (1958).

(17) C. Walling and R. B. Hodgdon, Jr., *ibid.*, **80**, 228 (1958); D. B. Denney and D. Z. Denney, *ibid.*, **82**, 1389 (1960).

(18) *Cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 242.

(19) Thus in contrast we have noted no spontaneous radical formation in the presence of simple alkenes, while styrene and acetylenes are not effective in inducing radical chain chlorinations; M. Poutsma, private communication.

(20) Unpublished experiments in these laboratories by M. Mintz.

Table VII. Relative Reactivities of Acetylenes and Olefins toward *t*-Butyl Hypochlorite^a

Substrate	Relative reactivity	
	Per molecule	Per H
Toluene (std.)	1.00	1.00
CH ₃ C≡CCH ₃	2.60 ± 0.16	1.3
CH ₃ CH=CHCH ₃ ^b	4.02	2.0
C ₆ H ₅ C≡CCH ₃	2.68 ± 0.04	2.7
C ₆ H ₅ CH=CHCH ₃	7.84 ± 0.5	7.8
C ₆ H ₅ C≡CCH ₂ CH ₃	6.75 ± 0.46	10.1
C ₆ H ₅ CH=CHCH ₂ CH ₃	12.5 ± 0.3	19
C ₆ H ₅ C≡CCH(CH ₃) ₂	11.4 ± 1.2	34
C ₆ H ₅ CH=CHCH(CH ₃) ₂	12.9 ± 0.3	39
C ₆ H ₅ CH ₂ C≡CC ₆ H ₅	30.6 ± 3	46
C ₆ H ₅ CH ₂ CH=CHC ₆ H ₅	19.8 ± 3.4	30
C ₆ H ₅ CH ₂ CH=CH ₂	4.63 ± 0.05	6.9

^a At 40°. ^b The *trans* isomer.²

dissociation energies for propargylic C–H bonds are slightly more than those for allylic C–H.²¹ On the other hand, in the phenylacetylene series, while acetylenes and olefins run roughly parallel, the relative reactivities of the acetylenes increase more rapidly with substitution. These results as far as we know are the first extensive comparison of the reactivities of propargylic hydrogens to radical attack.

Experimental

Materials, unless indicated, were commercial reagents, dried, distilled, and purity checked by g.l.c. *t*-Butyl hypochlorite was prepared by the method of Teeter and Bell,²² *t*-butyl hypobromite by a modification of the method of Geneste and Kergomard.²³ The following alkynes and alkenes were prepared by known methods, and purity and identity were checked by g.l.c. and n.m.r. spectra: *1*-phenylpropyne,²⁴ b.p. 183°, *n*²¹_D 1.5631; *1*-phenyl-1-butene,²⁵ b.p. 44° (1.5 mm.), *n*²¹_D 1.5508; *1*-phenyl-3-methyl-1-butene,²⁶ b.p. 109–110° (9 mm.), *n*²¹_D 1.5358; *1,3*-diphenylpropyne,²⁷ b.p. 136° (2 mm.), *n*²¹_D 1.6028; *1*-phenyl-1-butene, from benzaldehyde and *n*-propylmagnesium bromide²⁸ followed by dehydration over KHSO₄,²⁹ b.p. 190–192°, *n*²²_D 1.5390; *1*-phenyl-3-methyl-1-butene from benzaldehyde and isobutylmagnesium bromide²⁸ followed by KHSO₄ dehydration,²⁹ b.p. 201–203°, *n*²⁴_D 1.5298; *1,3*-diphenylpropene from β-phenylpropionaldehyde and phenylmagnesium bromide followed by KHSO₄ dehydration, b.p. 124° (1.1 mm.), *n*^{20,25}_D 1.5992.

Styrene reactions were carried out in a round-bottomed three-neck flask equipped with dropping funnel, thermometer, and condenser and stirred by a magnetic stirrer. The top of the condenser was connected to an ice trap, Dry Ice trap, and gas buret. Solvent and styrene were added to the flask and de-

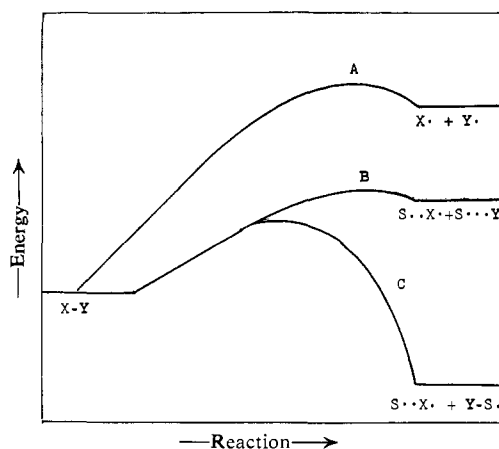


Figure 1. Schematic diagram of solvent effects on homolytic scission.

gassed at 10–20 mm. by alternate freezing and thawing. The flask was then frozen in liquid nitrogen, *t*-butyl hypochlorite (or hypobromite) was placed in the dropping funnel, and prepurified nitrogen was passed through the system. After warming to 0° in an ice bath the hypochlorite was added in small portions. Each addition led to a rapid rise in temperature (which was kept below 25°) and the system was allowed to cool to 0–5° before the next addition. Dark reactions were carried out in a darkened laboratory with the whole system wrapped in aluminum foil, using a dim flashlight to read temperature. Light reactions were illuminated by a 100-w. bulb at a distance of 6 in. Undegassed reaction mixtures showed an induction period before reaction while an experiment containing *t*-butylcatechol required warming to 50° before an exothermic reaction occurred. In the competitive reaction of styrene and cyclohexane, 0.42 *M* hypochlorite was added to 0.043 *M* styrene and 0.032 *M* cyclohexane. Reaction was less violent than in the case of pure styrene and relative reactivities were calculated from styrene consumed and cyclohexyl chloride produced (separated by g.l.c. and identified by infrared spectra).

Identification of Styrene Products. Small amounts (0–3%) of an unidentified gas collected in the gas buret in most reactions and in addition methyl chloride was detected by g.l.c. retention time in hypochlorite experiments. Acetone and *t*-butyl alcohol were identified by g.l.c. separation and infrared spectra and determined quantitatively by g.l.c. using internal standards calibrated against known mixtures. In addition, *t*-butyl hypobromite gave traces of two very low boiling products and a third with retention time (dinonyl phthalate column) slightly greater than *t*-butyl alcohol. Although *t*-butyl chloride was not formed initially in hypochlorite runs, it collected in quantity in a cold trap on vacuum distillation of crude reaction mixtures.

The main product of hypochlorite experiments, 2-phenyl-2-chloroethyl *t*-butyl ether, had been previously identified but its structure was further confirmed by n.m.r. spectra and by hydrogenolysis in absolute ethanol in the presence of PtO₂ and excess collidine to 2-phenylethyl *t*-butyl ether *Anal.* Calcd. for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 80.86;

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 (27) J. R. Johnson, T. L. Jacobs, and A. M. Schwartz, *J. Am. Chem. Soc.*, **60**, 1885 (1938).
 (28) D. Gauthier and P. Gauthier, *Bull. soc. chim. France*, **53**, 323 (1933).
 (29) J. W. Howard and W. A. Fraser, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 475.

H, 10.14. The infrared and n.m.r. spectra were identical with authentic material obtained by refluxing 2-phenylethanol, *t*-butyl chloride, and sodium carbonate for 48 hr. No ethylbenzene was produced by the hydrogenolysis. Phenyl-1,2-dichloroethane (styrene dichloride) was identified by thin layer chromatography and infrared spectrum after g.l.c. separation. N.m.r. spectra of crude reaction mixtures after removal of low boiling materials indicated small amounts of other products. Infrared spectra showed no carbonyl absorption but heating to 90° resulted in loss of ether absorption and formation of aldehyde. Addition of methanol led to no precipitation of polymer.

For quantitative analysis low boiling products were removed from weighted aliquots of reaction mixture under vacuum, a known amount of toluene was added as internal standard, and styrene and styrene dichloride were determined by g.l.c. A portion of the mixture (0.4–0.6 g.) was then added to 5 ml. of absolute ethanol, 1 ml. of collidine, and 120–130 mg. of PtO₂ and subjected to hydrogenolysis. Under these conditions the chloro ether was reduced as noted above, and blank experiments showed that styrene dichloride was quantitatively converted to ethylbenzene. The mixture was then analyzed for 2-phenylethyl *t*-butyl ether and ethylbenzene by g.l.c., and the excess ethylbenzene over that formed from the styrene present was taken as styrene dichloride. As noted earlier, this technique gives a somewhat higher value for dichloride, perhaps from reduction of more highly chlorinated products.

Reactions involving *t*-butyl hypobromite were analyzed similarly except that the major product, 2-phenyl-2-bromoethyl *t*-butyl ether, was determined by n.m.r. spectra using the area of the *t*-butoxy methyl singlet and the methyl singlet of added toluene standard. The ether was identified on the basis of the similarity of its infrared and n.m.r. spectra to that of the chloro ether above, its immediate reaction with alcoholic AgNO₃, and analysis. *Anal.* Calcd. for C₁₂H₁₉BrO: C, 56.04; H, 6.66. Found: C, 55.97; H, 6.32.

2-Butyne reactions in the absence of solvent were carried out essentially as with styrene, except that mixtures contained small known amounts of benzene and *o*-dichlorobenzene as internal standards for subsequent analysis. Addition of the first small amounts of hypohalite led to an immediate violent reaction with fuming of the solution, a rapid temperature rise, and separation of *t*-butyl alcohol as a cloudy suspension. The reaction became more moderate on further addition, the reaction mixture turned clear, and, although still pale yellow after 4 hr., gave no test for unreacted hypochlorite.

Reactions in CCl₄ were carried out in small pear-shaped flasks. Carbon tetrachloride–2-butyne was degassed and frozen in liquid N₂. Hypohalite, diluted with CCl₄, was added, and the system was flushed with nitrogen, closed with a wired-on stopper with stopcock, and placed in a room-temperature water bath. In light reactions with hypochlorite, reaction was complete in 1 hr. Dark systems examined after 1 hr. were still pale yellow. Hypobromite reactions were even more rapid, becoming colorless in 2–3 min. in the light.

A dark reaction in the presence of toluene was carried out similarly. Benzyl chloride was identified by infrared spectra after g.l.c. separation, and relative

reactivities, calculated from the 2-butyne consumed and benzyl chloride formed, agreed with those measured in light as described below.

Identification of 2-Butyne Products. Low boiling products from *t*-butyl hypochlorite included methyl chloride (identified by retention time), acetone, and *t*-butyl alcohol, determined as in the styrene system. The major product, 1-chloro-2-butyne, was identified by infrared spectrum (strong acetylene bands at 4.32 and 4.47 μ), n.m.r. spectrum (triplet at τ 8.16 and quartet at 5.87; methyl:methylene, 3:2), and analysis. *Anal.* Calcd. for C₄H₅Cl: C, 54.26; H, 5.69; Cl, 40.05. Found: C, 54.38; H, 5.55; Cl, 40.04. *trans*-2,3-Dichloro-2-butene was identified by elemental analysis and by comparison of its infrared and n.m.r. spectra and g.l.c. retention time with authentic material obtained by addition of chlorine to 2-butyne in CCl₄. Yields of both products were determined by g.l.c. (20% SF-96 silicone column programmed from 60 and 4°/min. vs. *o*-dichlorobenzene as internal standard. G.l.c. analysis indicated the presence of compound X and at least four other minor products. X appeared to be a dimer from retention time, had a 4:1.9 C–Cl ratio from analysis, and contained the ≡C–CH₂Cl function from its infrared spectrum, but was not completely identified.

t-Butyl hypobromite reaction mixtures were analyzed in a similar manner. 1-Bromo-2-butyne was identified from its infrared and n.m.r. spectra, both very similar to those of 1-chloro-2-butyne. *trans*-2,3-Dibromo-2-butene was separated by g.l.c., had the correct elemental analysis, and infrared and n.m.r. spectra were identical with authentic material.

Phenylalkyne reactions were carried out as above, although, as mentioned earlier, reactions were considerably slower. Acetone, *t*-butyl alcohol, and a gas with the g.l.c. retention time of methyl chloride were the sole, low boiling products obtained in any system and were determined as above.

N.m.r. spectra of reaction mixtures from 3-methyl-1-phenyl-1-butyne showed a single major product, with a singlet at τ 8.13. This product, considered to be 3-chloro-3-methyl-1-phenyl-1-butyne, was found to lose HCl on heating to yield 2-methyl-4-phenyl-3-buten-1-ene, C₆H₅C≡CC(CH₃)=CH₂. *Anal.* Calcd. for C₁₁H₁₀: C, 92.91; H, 7.09. Found: C, 92.94; H, 7.13. Infrared and n.m.r. spectra were consistent with this structure and the latter gave a methyl:methylene:phenyl ratio of 3.0:1.8:5.0. Two other small peaks on g.l.c. analysis showed the same retention time as authentic *cis*- and *trans*-1,2-dichloro-3-methyl-1-phenyl-1-butene. Although they underwent some decomposition on separation, infrared and n.m.r. spectra were consistent with these structures.

N.m.r. spectra of reaction mixtures from 1-phenyl-1-butyne (after removal of low boiling material) again showed a single major product with methyl doublet at τ 8.38 and 8.26, and a quartet centered at 5.25, ratio 3:1, consistent with the expected product, 3-chloro-1-phenyl-1-butyne. Yield was determined by comparison of the methyl triplet area with that of the unreacted 1-phenyl-1-butyne. Again, g.l.c. analysis showed two minor peaks corresponding to *cis*- and *trans*-1,2-dichloro-1-phenyl-1-butene.

The major product from 1-phenylpropyne was

Table VIII. Competitive Chlorinations^a

Compd. A	Compd. B	Relative reaction, A/B ^b
CH ₃ C≡CCH ₃	Toluene	2.60 ± 0.16 (3)
C ₆ H ₅ C≡CCH ₃	Toluene	2.86 ± 0.04 (2)
C ₆ H ₅ C≡CC ₂ H ₅	Toluene	6.75 ± 0.46 (2)
C ₆ H ₅ C≡CCH(CH ₃) ₂	Toluene	11.4 ± 1.2 (2)
Mesitylene	Toluene	4.32 ± 0.7 (3)
C ₆ H ₅ C≡CCH ₂ C ₆ H ₅	Mesitylene	7.06 ± 0.4 (3)
C ₆ H ₅ CH=CHCH ₂ C ₆ H ₅	Mesitylene	4.56 ± 0.95 (3)
C ₆ H ₅ CH ₂ CH=CH ₂	Mesitylene	1.07 ± 0.01 (2)
C ₆ H ₅ CH=CHCH ₃	Mesitylene	1.81 ± 0.10 (2)
C ₆ H ₅ CH=CHCH ₂ CH ₃	C ₆ H ₅ CH=CHCH ₃	1.60 ± 0.01 (2)
C ₆ H ₅ CH=CHCH(CH ₃) ₂	C ₆ H ₅ CH=CHCH ₂ CH ₃	1.03 ± 0.01 (2)

^a HO°. ^b Per molecule, number in parentheses is number of experiments and experimental error spread of duplicate or triplicate runs.

identified as 3-chloro-1-phenylpropyne by elemental analysis, and by infrared and n.m.r. spectra. *cis*- and *trans*-1,2-dichloro-1-phenylpropene were identified by g.l.c. retention time and n.m.r. spectra. Several other additional products were detected in minor amounts. Although the chief one appeared to be a dimer which lost HCl on heating, it was not further identified.

The authentic dichloro-1-phenylalkenes used in the above comparisons were prepared by chlorine addition to the corresponding acetylenes and separated by g.l.c. In each case the *trans* isomer was the major product, and stereochemistry was assigned on the basis of n.m.r. and infrared spectra. In n.m.r. spectra, *trans* isomers showed phenyl multiplets and *cis* isomers sharp singlets,³⁰ while in infrared spectra, *cis* isomers

showed strong absorption at 6.16 μ, virtually lacking in the *trans* compounds.³¹

Competitive experiments were run in sealed degassed tubes in CCl₄ solution (0.9–1.8 M in each hydrocarbon) containing suitable internal standards (chlorobenzene or *o*-dichlorobenzene) and irradiated in a 40° water bath, essentially as in previous work.² Under these conditions of dilution there was no fast dark reaction, and relative reactivities were calculated in the usual way² from g.l.c. analysis for unreacted hydrocarbons. Actual pairs investigated are listed in Table VIII.

(30) For comparison, aromatic protons of *cis*-stilbene yield a sharp singlet, while the *trans* isomer gives a doublet: D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind. (London)*, 1205 (1958).

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Reactions of Free, Ground-State Dichlorocarbene

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Dichlorocarbene was generated under vacuum by the pyrolysis of chloroform or carbon tetrachloride, at temperatures in the neighborhood of 1500°, and allowed to react with olefinic substrates on a liquid nitrogen cooled surface. The products are the expected 1,1-dichlorocyclopropanes. The additions to cis- and to trans-2-butenes were stereospecific. Free CCl₂, the precursor of these products, had been generated under spin relaxing conditions, thus indicating a singlet ground state.

Since all studies of the chemical properties of CCl₂ have been carried out in condensed phase, where association of the carbene with solvent or other Lewis bases may occur, one must conclude that the properties which have been reported may not be those of the free carbene. The recent report of Miller and Whalen that LiCCl₃ in ether is thermally¹ stable at -100° and yet reacts readily with cyclohexene to produce 7,7-dichloronorcaradiene raises with force the alternative

that a free carbene was not an intermediate in earlier studies. A parallel study, equally forceful toward this conclusion with reference to CHCl, has been reported by Closs and Coyle.² We have also noted a number of instances in which solvents affect the selectivities of carbenes.

The singlet designations for CX₂ were made to accord with the observations that additions to olefins were stereospecific and electrophilic in selectivity. Are these the properties of CX₂ or a complex?

Thus it became a matter of some urgency to examine the properties of CX₂ unambiguously free. This was accomplished by pyrolyzing CHCl₃ and CCl₄ (1500°) under high vacuum, where free flight from the generating source to the cold walls (-196°) was required to encounter an olefinic reactant. Under these circumstances the primary reactions must be attributed to the free carbene.

Three pyrolysis techniques were applied to chloroform and carbon tetrachloride thus providing a wide range of residence times in the pyrolysis zones: (a) allowing the vapors to enter a heated porous graphite

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(2) G. L. Closs and J. J. Coyle, *ibid.*, **84**, 4350 (1962).