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CHLORINATION STUDIES OF UNSATURATED MATERIALS IN NONPOLAR MEDIA—VI

PHOTOCHLORINATION OF 1-BUTYNE[1]

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Abstract—Treatment of neat 1-butyne with chlorine at −9° led to a negligible ionic or spontaneously-initiated free-radical reaction compared to 1-butene. However, photo-initiation led to production of seven products in the ratios shown: *trans*-1,2-dichloro-1-butene (Ia, 85–90%), *cis*-1,2-dichloro-1-butene (IIa, 2–3%), 3-chloro-1-butyne (VI, 3–5%), 1-chloro-1,2-butadiene (VII, 1%), 4-chloro-1-butyne (VIII, 2–3%), *cis*-1-chloro-1-butene (IV, 1–3%) and 2-chloro-1-butene (III, <1%). No significant effects of 1-butyne or chlorine concentration were observed. Products Ia and IIa are formulated as the result of largely *trans* addition (Ia/IIa ~0·7 at equilibrium); products VI and VII as the result of hydrogen abstraction from C-3 followed by chain transfer of the resulting propargylic radical with chlorine at both termini; product VIII as the result of hydrogen abstraction from C-4; and products III and IV as the result of interception of a certain fraction of vinyl radicals (produced by addition) by hydrogen chloride rather than chlorine. The relative reactivities of each of the reactive positions were determined by competitive experiments with cyclohexane.

INTRODUCTION

CHLORINATION of nonfunctionalized olefins in nonpolar solvents may follow either an ionic or spontaneously-initiated free-radical pathway.[2] Ionic reaction can always be isolated by use of radical inhibitors such as oxygen;[2c] in the absence of inhibitors, however, the reaction course is a function of olefin structure and concentration.[1,2b] These findings suggested a parallel study of chlorination of simple alkynes. Although addition of chlorine to triple bonds is a standard textbook reaction, surprisingly few quantitative data exist for substrates more complex than acetylene itself.[3] Leitch[4] reported that treatment of gaseous propyne with excess chlorine at 65–70° gave 1,1,2,2-tetrachloropropane and *trans*-1,2-dichloropropene in 60–65% and 15–20% yield, respectively; it is not clear whether reaction was truly vapor-phase or whether it occurred in liquid films of products on the walls.[5] In a parallel study[6] both *trans*-dichloroolefins and saturated tetrachlorides were isolated from chlorination of 1-butyne, 2-butyne and 1-pentyne; lesser amounts of unidentified substitution products were also produced. Single and double chlorine addition to 1-hexyne in the presence of antimony pentachloride as catalyst has been reported.[7] The present paper describes a study of liquid-phase chlorination of 1-butyne as a model for terminal acetylenes.

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[1] For previous paper see: M. L. Poutsma, *J. Amer. Chem. Soc.* **87**, 4293 (1965).

[2a] M. L. Poutsma, *J. Amer. Chem. Soc.* **87**, 2161 (1965); [b] *Ibid.* **87**, 2172 (1965); [c] *Ibid.* **87**, 4285 (1965).

[3] J. A. Nieuwland and R. R. Vogt, *The Chemistry of Acetylene* p. 101. Reinhold, New York (1945).

[4] L. C. Leitch, *Canad. J. Chem.* **31**, 385 (1953).

[5] For a comparable situation with olefins, cf. H. P. A. Groll, G. Hearne, F. F. Rust and W. E. Vaughan, *Ind. Eng. Chem.* **31**, 1239 (1939).

[6] A. T. Morse and L. C. Leitch, *Canad. J. Chem.* **33**, 6 (1955).

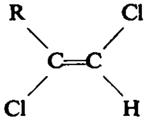
[7] G. F. Hennion and C. E. Welsh, *J. Amer. Chem. Soc.* **62**, 1367 (1940).

RESULTS

Passage of gaseous chlorine (< 5 mole %) diluted with oxygen into liquid 1-butyne at −9° in the dark led to negligible reaction even after 1 hr. Such behavior is in marked contrast to that of 1-butene which reacted with chlorine under identical conditions almost as rapidly as it was introduced;[2b] in fact, competitive experiments with mixtures of 1-butene and 1-butyne suggested that the former was $>10^2$ more reactive under these conditions.

Replacement of the oxygen atmosphere by nitrogen generally gave little, if any, rate enhancement as long as illumination was rigidly excluded; however, occasionally and unpredictably, reaction was found to have proceeded significantly after 5–10 min in the dark. In contrast, illumination by a sunlamp through Pyrex consistently led to almost instantaneous reaction; (it is noteworthy, however, that the product distribution from those few spontaneous dark reactions was not significantly different from that from the photo-initiated runs). The results in the remainder of this section are derived from the photo-initiated radical reaction.

GLC analysis of reaction mixtures showed one major product (ca. 90% of the total) and 7 minor products (A–G in order of increasing retention time), all but one of which were more volatile than the major product. This predominant product, isolated by distillation, had physical properties comparable to those of the dichloride isolated by Morse and Leitch[6] and assigned as *trans*-1,2-dichloro-1-butene (Ia). These authors obtained both geometrical isomers of 1,2-dichloro-1-butene (Ia and IIa) from dechlorination of 1,1,2,2-tetrachlorobutane with zinc and assigned stereochemistry by assuming a parallelism in boiling point and refractive index with the corresponding isomers in the C-3 series.[8] In the latter, the less symmetrical *cis* stereochemistry (IIb) had been assigned to the isomer with the greater dipole moment[9] and more intense IR band (1614 cm^{-1}) associated with the C=C stretching mode.[10] In our hands the lower-boiling isomer from the zinc dechlorination (identical with the major chlorination product from 1-butyne) exhibited essentially no IR absorption in the 1750–1600 cm^{-1} region whereas the higher-boiling isomer showed a medium-intensity band at 1615 cm^{-1}. Hence the previous assignment[6] is confirmed and the major chlorination product is indeed Ia.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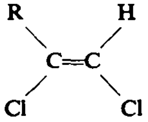
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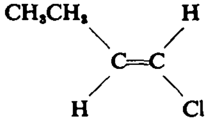
V

a. R = C_2H_5
b. R = CH_3

Minor products A–G were each isolated by preparative GLC and structural assignments made as shown in the Experimental for all except C which was barely detectable and never made up >0·1% of the total products. In brief, product A was a terminal olefin identical with commercially available 2-chloro-1-butene (III). On the

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[8] L. C. Leitch, personal communication.

[9] W. H. King and H. A. Smith, *J. Amer. Chem. Soc.* 72, 3459 (1950).

[10] H. J. Bernstein and J. Powling, *J. Amer. Chem. Soc.* 73, 1843 (1951).

basis of spectral evidence, product B was assigned as *cis*-1-chloro-1-butene (IV); commercially available 1-chloro-1-butene was largely the *trans* isomer (V) which could not be detected in the chlorination mixture (<10% of IV). Treatment of 3-butyn-2-ol with thionyl chloride in the presence of pyridine has been shown to produce 3-chloro-1-butyne (VI) and 1-chloro-1,2-butadiene (VII);[11] these products were shown to be identical with D and E. Product F was 4-chloro-1-butyne (VIII) which can be prepared by treatment of 3-butyn-1-ol with thionyl chloride.[12] Finally, product G was IIa. The retention times of the chlorination products on two different GLC columns were identical with those of authentic materials in all cases (except IV for which authentic material was not prepared but whose assignment rests on NMR evidence which appears to be essentially unique for this material).

A series of runs was conducted to determine the effects of reaction variables (Table 1). The reactant solution (1-butyne and 1,1,2-trichlorotrifluoroethane diluent) was flushed well with nitrogen and then the appropriate amount of chlorine was introduced as a gas in 1–3 min in the dark. Subsequent illumination led to rapid decoloration; occasional runs which proceeded in the dark are so noted. GLC analysis gave relative molar quantities of Ia, IIa, III, IV, VI, VII and VIII which have been normalized to 100%; this procedure ignores trace quantities both of product C and poly-chlorination products. Entries 1–8 were designed to determine the effect of changing 1-butyne concentration at constant initial chlorine concentration.[13] The results show some scatter which is not surprising since rather small GLC areas had

TABLE 1. PRODUCT DISTRIBUTIONS FROM PHOTOCHLORINATION OF 1-BUTYNE AT −9° IN A NITROGEN ATMOSPHERE

Entry	$(\text{Butyne})_0^a$	$(Cl_2)_0^a$	$III^{b,c}$	$IV^{b,c}$	$VI^{b,c}$	$VII^{b,c}$	$VIII^{b,c}$	$Ia^{b,c}$	$IIa^{b,c}$
1	12·4	0·09	0·6	1·3	5·2	1·2	1·9	86·7	3·1
2[d]	9·9	0·09	0·2	0·4	3·2	0·9	1·6	90·8	2·9
3[d]	9·9	0·09	0·5	0·7	3·6	1·1	2·0	89·2	3·0
4	7·4	0·09	0·5	1·4	4·1	1·1	2·0	87·8	3·0
5	4·9	0·09	1·0	3·2	5·5	1·6	2·0	84·0	2·7
6	2·5	0·09	0·3	1·4	4·2	1·1	1·6	88·6	2·7
7	1·2	0·09	0·3	1·5	4·3	1·1	2·3	88·0	2·5
8	0·6	0·09	0·4	2·1	4·1	1·0	2·6	87·5	2·4
9[e]	1·2	0·09	1·1	4·3	5·5	1·5	3·0	81·8	2·9
10[e]	1·2	0·09	1·0	4·2	5·4	1·4	2·6	82·7	2·6
11	3·7	0·13	0·3	1·1	4·1	1·1	2·2	88·6	2·6
12	3·7	0·20	0·3	1·3	4·3	1·2	2·2	88·0	2·8
13	3·7	0·26	0·6	2·5	4·3	1·1	2·1	87·1	2·3
14[d]	3·7	0·29	0·3	1·0	4·3	1·1	2·2	88·4	2·8
15[f]	3·7	0·07	6·0	34·8	7·7	2·2	3·5	43·7	2·1
16[f]	3·7	0·07	4·1	23·7	6·1	2·3	2·9	59·1	2·0
17[g]	3·7	0·07	0·2	0·2	5·2	1·5	1·9	88·5	2·5

[a] Initial molar concentration in $C_2F_3Cl_3$. [b] III = 2-chloro-1-butene; IV = *cis*-1-chloro-1-butene; VI = 3-chloro-1-butyne; VII = 1-chloro-1,2-butadiene; VIII = 4-chloro-1-butyne; Ia = *trans*-1,2-dichloro-1-butene; IIa = *cis*-1,2-dichloro-1-butene. [c] Mole% normalized to 100% for the 7 products listed; see text. [d] Reaction proceeded without illumination. [e] Reaction mixture illuminated during Cl_2 addition. [f] Reaction mixture saturated with HCl. [g] Solid Na_2CO_3 present.

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

[12] A. C. Cope and D. F. Rugen, *J. Amer. Chem. Soc.* **75**, 3215 (1953).

[13] To avoid secondary reactions, $(\text{1-butyne})_0 \gg (\text{chlorine})_0$ in all cases.

to be determined (e.g., in a typical run, III made up ca. 50 ppm of the solution being analyzed); however, no trends were apparent for any of the 7 products. The two runs which proceeded without illumination (entries 2 and 3) seem to be characterized by slightly greater amounts of addition product Ia at the expense of vinyl chlorides III and IV. Entries 5–6 and 11–14 show a parallel series of runs with varying initial chlorine concentration at constant 1-butyne concentration; again no significant effects appear. Illumination during chlorine introduction (and hence very low average chlorine concentration compared to the other runs) tended to increase III and IV at the expense of Ia but had negligible effect on the Ia:IIa ratio (entries 9 and 10). If the nitrogen carrier gas was replaced by hydrogen chloride (entries 15 and 16), a dramatic increase in (III + IV) from ca. 2% to 30–40% occurred while (Ia + IIa) decreased from ca. 90% to 45–60%; on the other hand, chlorination under nitrogen in the presence of solid sodium carbonate (entry 17) gave results characterized by the lowest value of (III + IV) encountered in this study. Illumination of 1-butyne in the presence of hydrogen chloride and nitrogen alone (no added chlorine) under conditions of the chlorination experiments gave no products detectable by GLC analysis even after reaction times much longer than needed for a typical chlorination.

TABLE 2. PRODUCT DISTRIBUTIONS FROM PHOTOCHLORINATION OF 1-BUTYNE—CYCLOHEXANE MIXTURES AT −9° IN A NITROGEN ATMOSPHERE

(Butyne)$_0$[a]	(C_6H_{12})$_0$[a]	(Cl_2)$_0$[a]	VI[b,c]	VII[b,c]	VIII[b,c]	Ia[b,c]	IIa[b,c]	IX[b,c]	k_a[d]	k_{t3}[d]	k_{t4}[d]
2·5	7·4	0·09	4·1	1·1	1·5	100·0	—	388·0	9·7	0·24	0·047
2·5	7·4	0·07	4·1	1·1	1·8	100·0	4·0	360·0	10·5	0·26	0·058
6·2	4·6	0·07	4·9	1·4	1·8	100·0	3·4	117·0	8·0	0·24	0·046
6·2[e]	4·6	0·09	4·7	1·3	1·7	100·0	3·0	99·0	9·4	0·27	0·050
8·3[e]	1·9	0·09	4·1	1·3	1·9	100·0	4·5	23·4	12·5	0·32	0·076
8·3	1·9	0·07	5·7	1·7	2·2	100·0	4·2	36·9	7·9	0·27	0·054
									9·7[f]	0·27[f]	0·055[f]

[a] Initial molar concentration. [b] VI = 3-chloro-1-butyne; VII = 1-chloro-1,2-butadiene; VIII = 4-chloro-1-butyne; Ia = *trans*-1,2-dichloro-1-butene; IIa = *cis*-1,2-dichloro-1-butene; IX = chlorocyclohexane. [c] Relative molar amount compared to Ia assigned as 100·0. [d] See Discussion for definition and determination of k's. [e] Reaction proceeded without illumination. [f] Mean value.

A series of runs was conducted in similar fashion with cyclohexane as the diluent; the ratio of hydrocarbons was varied by a factor of 13. Products derived from 1-butyne (except minor products III and IV which were obscured by the cyclohexane band) as well as chlorocyclohexane (IX) were again determined by GLC analysis; results are listed in Table 2.

Dichlorobutenes Ia and IIa did not appear to be interconverted during chlorination runs since their ratio did not depend on the extent of conversion. However, treatment of either of the dichlorides with a catalytic amount of thiophenol in refluxing hexane with illumination gave an equilibrium mixture containing 58–59% of IIa.

Photo-initiated reaction of 1-butyne with t-butyl hypochlorite to low conversion gave a reaction mixture in which 3-chloro-(VI) and 4-chloro-1-butyne (VIII) and allenic chloride VII could be determined by GLC analysis. For two runs, the ratio (VI):(VII) was 11·1 ± 0·7 and the ratio (VI + VII):(VIII) was 435 ± 15.

DISCUSSION

The relative inertness of 1-butyne towards chlorine under oxygen (radical-inhibited conditions) compared to 1-butene is in accord with the usual observation that alkynes react with electrophilic reagents more slowly than corresponding alkenes.[14] Removal of the inhibitor without supplying external radical initiation gave erratic results in that only occasional runs proceeded at a modest rate while most still showed negligible reaction. Thus, while some spontaneous initiation of radical reactions may occur,[2a] it is obviously less efficient for 1-butyne than for the corresponding olefin, 1-butene.[2b,15] Chlorine thus behaves in marked contrast to t-butyl hypochlorite which has been found by Walling *et al.*[16] to produce radicals by reaction with certain acetylenes and styrene[17] but not with alkylated olefins.

The photo-initiated reaction proceeds by means of a chlorine atom chain and radical intermediates. Chlorine atom has been shown to react with olefins by competitive addition and hydrogen abstraction[2a,b] and similar behavior would be expected for acetylenes. Addition of chlorine atom to 1-butyne and subsequent chain transfer with chlorine molecule leads to dichlorides Ia and IIa with the observed *trans*:*cis* ratio of 32 ± 3. This ratio is kinetically controlled since the thermodynamic ratio was shown to be 0·7 by the equilibration study. More detailed consideration of the position of attack and of the mechanistic origin of the observed stereochemistry will be deferred until the source of vinyl chlorides III and IV is considered (*vide infra*). In a second primary step, chlorine atom abstracts a propargylic hydrogen atom to produce radical X which leads to propargylic chloride VI and allenic chloride VII in a ratio of 3·8 ± 0·2. Propargylic radicals have not been extensively studied and this seems to be the first demonstration of chain transfer of such a radical to give allenic as well as propargylic products. Coupling of allenyl radical ($CH_2{=}C{=}\dot{C}H \leftrightarrow \dot{C}H_2{-}C{\equiv}CH$) with methyl radical has been reported[18] to give 1,2-butadiene as well as 1-butyne. Reaction of 1-butyne with t-butoxy radical derived from t-butyl hypochlorite should also produce radical X; chain transfer of X with t-butyl hypochlorite is observed to be less favorable for allene production (VI:VII = 11). Finally, 4-chloro-1-butyne (VIII) is the expected product from abstraction of the terminal saturated hydrogen atom via radical XI.

The more unusual products were vinyl chlorides III and IV. Formally, these are the result of addition of hydrogen chloride produced by the abstraction reactions leading to VI–VIII; however, control experiments showed that no detectable polar nor photo-initiated reaction of hydrogen chloride with 1-butyne occurred under the present reaction conditions in the absence of chlorine. If one notes that the major vinyl chloride is terminal in orientation, then a more plausible explanation is that a vinyl radical produced by addition of chlorine atom to the triple bond is partially

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[14] P. B. D. de la Mare, *Quart. Revs.* 3, 133 (1948) and L. F. and M. Fieser, *Organic Chemistry* (3rd Edition) p. 88. Reinhold, New York (1956). Cf., however, D. S. Noyce, M. A. Matesich, M. D. Schiavelli and P. E. Peterson, *J. Amer. Chem. Soc.* 87, 2295 (1965).

[15] It is not likely that slow radical reaction is the result of a slow chain-transfer step since dark chlorination of mixtures of 1-butene and 1-butyne proceeded rapidly to give comparable amounts of products from each; cf. Ref. 2*a* for a discussion of kinetics.

[16] C. Walling, L. Heaton and D. D. Tanner, *J. Amer. Chem. Soc.* 87, 1715 (1965).

[17] Dark chlorination of styrene follows a predominantly ionic pathway; M. L. Poutsma, unpublished results.

[18] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.* 39, 2147 (1963).

diverted from forming dichloride by reaction with some hydrogen atom donor. Several observations implicate hydrogen chloride (rather than starting material or some product) as this source: (1) products III and IV are reduced substantially by addition of sodium carbonate to remove hydrogen chloride as it is formed; (2) these products are strongly enhanced from 1–3% to 30–40% of the total products by addition of excess hydrogen chloride; and (3) these products are somewhat greater in runs in which illumination was supplied during chlorine introduction, conditions under which the average chlorine concentration was lower than usual while the average hydrogen chloride concentration should not have been greatly affected. In a variety of runs without added hydrogen chloride, the ratio (Ia + IIa):(III + IV) was in the range 15–100 while the sum (Ia + IIa + III + IV) was 92 ± 1% of the total products; addition of hydrogen chloride reduced the ratio markedly to 1–2 but altered the sum only slightly (88 ± 1%). Such behavior is additional evidence that the product pairs (Ia + IIa) and (III + IV) arise from a common intermediate. In contrast to the well-known anti-Markownikoff addition of hydrogen bromide to olefins,[19a] radical-chain addition of hydrogen chloride to olefins is an unfavorable process at best because the reaction of a typical secondary alkyl radical with hydrogen chloride is endothermic by 9 kcal/mole.[19b] Thus radical chlorination of simple olefins does not give detectable amounts of saturated monochlorides even though hydrogen chloride is produced.[2] However, attack of a vinyl radical on hydrogen chloride to produce a vinyl C—H bond and chlorine atom should be a nearly thermoneutral process since $D_{(H—Cl)} = 103$ kcal/mole[19c] and $D_{(CH_2{=}CH—H)} = 105 \pm 3$ kcal/mole.[20] Hence competitive reactions of a vinyl radical with chlorine and hydrogen chloride are not unreasonable.

If this hypothesis concerning the source of the vinyl chlorides is correct, then a portion of nonterminal addition of chlorine atom to 1-butyne to produce radical XII (along with the expected radical XIII[21]) is implied by formation of III. A similar situation has been suggested[2b] to explain the relative reactivity data for addition of chlorine atom to olefins. Unfortunately, one cannot determine the relative rates of production of radicals XII and XIII from the amounts of III and IV produced since their relative reactivities towards chlorine and hydrogen chloride may well be different.

At least two cases of radical addition to terminal acetylenes have been studied in detail with respect to stereochemistry under conditions where any post-isomerization was accounted for. Hydrogen bromide and propyne give >99% *trans* addition[22] while thiolacetic acid and 1-hexyne give an 88:12 *trans*:*cis* ratio.[21] Radical addition to an acetylene produces a vinyl radical whose ground state appears to be bent on the basis of ESR evidence[18,23] and which can thus exhibit *cis–trans* isomerism. The observed stereochemistry is the result of a combination of factors such as the stereospecificity of the initial addition step, the energy barrier to inversion of the vinyl radical, and the relative rates of chain-transfer of the isomeric radicals with addend; the ensuing kinetic situations have been outlined clearly by Kampmeier and Chen.[21] Unfortunately

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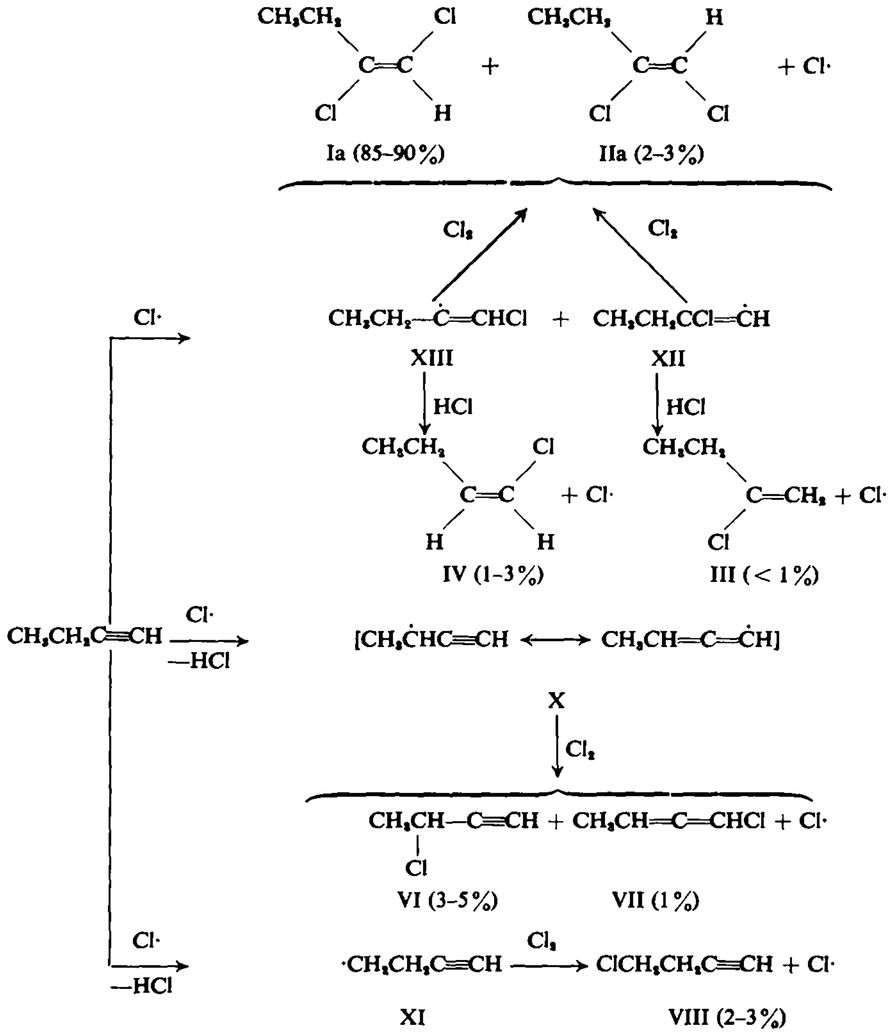
[19] C. Walling, *Free Radicals in Solution* [a] pp. 291–296; [b] p. 286; [c] pp. 48–50. Wiley New York (1957).

[20] A. G. Harrison and F. P. Lossing, *J. Amer. Chem. Soc.* **82**, 519 (1960).

[21] See J. A. Kampmeier and G. Chen, *J. Amer. Chem. Soc.* **87**, 2608 (1965) for a recent review of radical additions to acetylenes.

[22] P. S. Skell and R. G. Allen, *J. Amer. Chem. Soc.* **80**, 5997 (1958) and **86**, 1559 (1964).

[23] E. L. Cochran, F. J. Adrian and V. A. Bowers, *J. Chem. Phys.* **40**, 213 (1964).



occurrence of a significant fraction of nonterminal addition and hence of two distinct pathways for addition of chlorine to 1-butyne nullifies any attempt to determine uniquely the degree of stereospecificity of each pathway. Thus while the sum of the two pathways gives $>96\%$ *trans* addition, the pathway initiated by terminal attack proceeding through radical XIII may be even more stereoselective. That is, the small amount of *cis* product IIa may have arisen largely from radical XII, the product of nonterminal addition. As a rationale for this possibility, it should be noted that 1-alkylvinyl radicals (e.g. XIII) have been shown in ESR studies to have significantly longer inversion lifetimes than 1-hydrovinyl radicals (e.g. XII) possibly because of tunneling in the latter case.[18] The observed *trans*:*cis* ratio does not appear to be a function of chlorine concentration so that, in any case, we are not dealing with the "intermediate case" discussed by Kampmeier and Chen.[21] Finally, the production of IV (but not V) by radical hydrogen chloride addition to 1-butyne is as expected if radical XIII is produced mainly with the ethyl and chloro groups *cis* and then reacts with chlorine or hydrogen chloride more rapidly than it inverts.

The measurements listed in Table 2 allow us to compare relative rates of addition and abstraction by chlorine atom for 1-butyne with the corresponding values for 1-butene.[2b] Literature values for methyl radical,[24a] trifluoromethyl radical,[24b] and poly-(methylacrylate) or -(acrylonitrile) radical[24c] suggest that radicals add to alkynes some 1–5 times more slowly than to similarly substituted alkenes; in particular, propyne is one-half as reactive towards methyl radical as propene at 65°.[24a] Hence the value of $k_a = 9{\cdot}7$ for 1-butyne (relative rate constant for addition of chlorine atom compared to $k_t = 1{\cdot}00$ for abstraction of a single cyclohexyl hydrogen atom) as compared with $k_a = 11{\cdot}7$ for 1-butene is not surprising for the generally unselective chlorine atom.[25] With respect to hydrogen abstraction, propargylic hydrogen atoms in a number of terminal alkynes appear to be slightly more reactive than corresponding allylic ones towards methyl radical at 65°;[24a] the hydrogens of 1-butene and 1-butyne have been reported as equally reactive towards methyl radical at 182°.[26] Walling *et al.*,[16] found propargylic hydrogen atoms to be 35–150% as reactive as their allylic counterparts towards t-butoxy radicals at 40°. For 1-butyne, k_{t3}, the relative rate constant for abstraction of a single hydrogen atom from C-3 compared to $k_t = 1{\cdot}00$ for a single cyclohexyl hydrogen atom, for the propargylic hydrogen atom is only one-third that for the allylic hydrogen atom even though the latter is *not* activated compared with an ordinary secondary hydrogen atom.[2b] Also, k_{t4}, the relative rate constant for abstraction of a single hydrogen atom from C-4, is only 0·055 compared with 0·27 for the saturated hydrogen atom of 1-butene[2b] and 0·37 for that in 2,3-dimethylbutane.[27] The magnitude of this deactivating effect of the triple bond is surprising and deserves further study. The internal consistency of the data is shown by the fact that the k values determined from 1-butyne-cyclohexane mixtures predict a ratio of (Ia + IIa):(VI + VII):(VIII) of 97:5·4:2·0 whereas the average of entries 1–14 of Table 1 is 90:5·6:2·2.

EXPERIMENTAL

IR spectra were determined as 10% CS_2 solns on a Beckman IR-5A instrument; NMR spectra were determined as 20% CCl_4 solns on a Varian A-60 instrument and results expressed in ppm downfield from internal TMS; b.ps are uncorrected.

Materials. 1-Butyne (Farchan Research Laboratories) was distilled through an 18-inch glass helix-packed column in a 4°-room, and a center cut, b.p. 8°, was retained and stored in a small cylinder. HCl (Matheson) was used as received. Treatment of 1,1,2-trichlorotrifluoroethane, N_2 and O_2 has been described previously.[2a]

Product isolation and identification. 1-Butyne (57 ml, 0·70 mole) was collected in a flask equipped with a stirrer, Dry Ice reflux condenser, drying tube, and gas inlet tube. After the butyne was flushed with N_2 at 0°, Cl_2 (12·5 ml liquid, 0·28 mole), which had been collected in a calibrated trap, was allowed to vaporize into the N_2 stream and be swept into the reaction vessel. The flask was illuminated with 2-275 w. sunlamps during the 30-min Cl_2 introduction period. The ice bath was removed, the Dry Ice reflux condenser was replaced by a water-cooled reflux condenser, and excess butyne was allowed to vaporize in a N_2 stream. GLC analysis (conditions below) of the liquid residue showed a

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[24a] M. Gazith and M. Szwarc, *J. Amer. Chem. Soc.* **79**, 3339 (1957); [b] A. P. Stefani, L. Herk and M. Szwarc, *Ibid.* **83**, 4732 (1961); [c] K. W. Doak, *Ibid.* **72**, 4681 (1952).

[25] Since minor products III and IV were not included in the calculation of k_a, it may be slightly low; see Experimental.

[26] E. W. R. Steacie, *Atomic and Free Radical Reactions*, p. 500. Reinhold, New York (1954).

[27] G. A. Russell, A. Ito and D. G. Hendry, *J. Amer. Chem. Soc.* **85**, 2976 (1963).

major band of retention time expected for a C-4 dichloride, 6 minor bands of shorter retention time labelled A–F, a minor band of somewhat longer retention time labelled G, and several bands of considerably longer retention time. These latter bands did not appear to a significant extent if the conversion was kept $<5\%$; therefore no attempt was made to identify the secondary products. Distillation of the liquid residue gave: (1) 1·9 g of a mixture, b.p. <92°, which was used to isolate A–F by preparative GLC; (2) 5·4 g, b.p. 92–99°, 95% the major product by GLC analysis; (3) 10·2 g, b.p. 99–100°, n_D^{23} 1·4509, 99% the major product; (4) 1·0 g of a mixture, b.p. 35–56° (22 mm), which was used to isolate G by preparative GLC; and (5) ca. 10 g of residue whose GLC analysis gave the peaks characteristic of secondary products. The major product was transparent in the IR from 1750–1600 cm^{-1}, showed NMR bands at 6·10 ppm (singlet), 2·55 ppm (quartet, J = 7·5 c/s), and 1·15 ppm (triplet) with relative areas of 1·03:1·97:3·00, was identical with the lower-boiling product from Zn dechlorination of 1,1,2,2-tetrachlorobutane (*vide infra*), and was therefore assigned as *trans*-1,2-*dichloro*-1-*butene* (Ia) (lit.[6] b.p. 99·5–100·5°, n_D^{20} 1·4522). Product A showed very strong IR bands at 1635 and 880 cm^{-1} which suggested an unsymmetrical terminal olefin.[28a] 2-*Chloro*-1-*butene* (III) (Columbia Organic Chemicals) was purified by distillation and preparative GLC to give a sample, b.p. 57·5°, n_D^{23} 1·4096 (lit.[29] b.p. 57–59°, n_D^{21} 1·4115), whose IR spectrum was identical with that of A; the NMR spectrum confirmed the structure: 5·10 ppm (narrow multiplet), 2·38 ppm (quartet with additional fine structure, J = 7 c/s), and 1·15 ppm (triplet) with relative areas of 2·02:2·02:2·96. Product B showed C═C stretch in the IR spectrum at 1630 cm^{-1} (m) but was transparent in the 1000–925 cm^{-1} region (*trans* H—C═C—H).[28a] The NMR spectrum showed absorption at 5·80 ppm (multiplet), 2·20 ppm (multiplet), and 1·10 ppm (triplet, J = 7·5 c/s) with relative areas of 1·92:2·03:3·05; the low-field multiplet could be analyzed as an ABX$_2$ pattern to yield J_{AB} = 7·2 c/s as expected for *cis* vinylic protons. Hence B is assigned as cis-1-*chloro*-1-*butene* (IV). Commercial 1-chloro-1-butene (Columbia Organic Chemicals) was predominantly a different compound of higher boiling point[29b] with IR bands at 1640 cm^{-1} (m) and 935 cm^{-1} (vs)[28a] and an NMR spectrum similar to that of B but with J_{AB} = 13·2 c/s; this evidence is consistent with the *trans* structure. Product C has not been identified. Product D, n_D^{24} 1·4206, had an IR spectrum identical with that of authentic 3-*chloro*-1-*butyne* (VI) (*vide infra*) (lit.[11] n_D^{25} 1·4219) and a consistent NMR spectrum: 4·59 ppm (quartet of doublets), 2·52 ppm (doublet, J = 2·3 c/s), and 1·76 ppm (doublet, J = 6·85 c/s). Product E had an IR spectrum (1965 cm^{-1})[28b] identical with that of authentic 1-*chloro*-1,2-*butadiene* (VII) (*vide infra*) and an NMR spectrum in agreement with that reported.[30] Product F had an IR spectrum (3310 cm^{-1} (s) and 2125 cm^{-1} (vw)[28b]) identical with that of authentic 4-*chloro*-1-*butyne* (VIII) (*vide infra*) and NMR bands at 3·58 ppm (triplet, J = 7 c/s), 2·65 ppm (triplet of doublets), and 2·01 ppm (triplet, J = 2·5 c/s). The higher-boiling isomer from zinc dechlorination of 1,1,2,2-tetrachlorobutane (*vide infra*) proved to be identical with product G and is assigned as *cis*-1,2-*dichloro*-1-*butene* (IIa).

Preparation of authentic materials. To 81 ml (1·0 mole) of 1-butyne was added 142 g (2·0 moles) Cl$_2$ at 0° with illumination in the manner described above. Distillation gave 12·4 g, b.p. 76–84° (29 mm), n_D^{23} 1·4867, 79% pure by GLC analysis, and 75·4 g, b.p. 84–86° (29 mm), n_D^{23} 1·4888, >95% pure, of 1,1,2,2-tetrachlorobutane (lit.[6] b.p. 85–85·5° (25 mm.), n_D^{20} 1·4908). Treatment of this tetrachloride with Zn[6] followed by distillation gave ca. 95% pure samples of Ia and IIa; preparative GLC was used to obtain pure samples of each. The physical and spectral properties of the *trans* isomer are given above; the *cis* isomer, n_D^{24} 1·4581 (lit.[6] n_D^{20} 1·4598), showed IR absorption at 1615 cm^{-1}, and had NMR bands at 6·17 ppm (triplet, J = 1·2 c/s), 2·43 ppm (quartet of doublets) and 1·16 ppm (triplet, J = 7·5 c/s). Treatment of 3-butyn-2-ol with SOCl$_2$ in diethyl carbitol according to the method of Jacobs *et al.*[11] and distillation of the volatile products gave a mixture whose GLC spectrum showed two bands of approximately equal size. Preparative GLC afforded pure samples of VI, n_D^{24} 1·4198, with all IR bands corresponding to those reported[11] and of VII, n_D^{24} 1·4710. Reaction between 3-butyn-1-ol and SOCl$_2$[12] gave VIII, b.p. 85–86°, n_D^{24} 1·4380 (lit.[12] b.p. 84–85°, n_D^{25} 1·4376).

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[28] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (2nd Edition) [a] p. 34. [b] p. 58; Wiley New York (1958).

[29a] J. W. Kroeger, F. S. Sowa and J. A. Nieuwland, *J. Org. Chem.* **1**, 163 (1936); [b] L. Navez, *Bull. Soc. Chim. Belges* **39**, 442 (1930).

[30] S. L. Manatt and D. D. Elleman, *J. Amer. Chem. Soc.* **84**, 1579 (1962); E. I. Snyder and J. D. Roberts, *Ibid.* **84**, 1582 (1962).

Quantitative chlorination procedure. The results in Table 1 were obtained by the general procedure outlined previously.[3a,b] The appropriate amount of 1-butyne was condensed into the reaction vessel by use of a Dry Ice condenser. Cl_2 introduction was carried out in the dark except where noted and subsequent illumination was provided by a 275-w. sunlamp at 9–12 inches. The GLC analyses were performed directly on reaction mixtures without prior workup with a (Micro-Tek 2500 R instrument equipped with 2-m Perkin–Elmer "R" columns (polypropylene glycol) and a flame ionization detector. Injections were performed with a pressure-tight 1μl sampler (Micro-Tek Snap Sampler) or a precooled syringe. Correlation of product identities and retention times was also checked on column "O" (silicone grease). At 58° and a He flow of ca. 200 ml/min, retention times in min were: III, 3·1; IV, 3·8; VI, 7·1; VII, 8·7; VIII, 10·6; Ia, 12·0; and IIa, 26·0. All areas were determined from the product of peak height and retention time and were corrected to molar quantities by use of calibration factors determined from analyses of standard mixtures of authentic materials.

TABLE 3. EQUILIBRATION OF 1,2-DICHLORO-1-BUTENES IN HEXANE AT 65–70°[a]

Time, hr	% *cis* isomer From *trans*	 From *cis*
0	2	99
1	31	76
17	51	62
23	54	60
49	55	59
73	57	60
155	58	59

[a] Solution 0·16M in olefin and 0·05M in thiophenol irradiated with sunlamp through Pyrex.

Relative reactivity measurements. The values reported in Table 2 for competitive experiments with cyclohexane were performed in identical fashion except that IX, retention time 42 min, was also determined. Because of interference from the cyclohexane band, products III and IV could not be determined and hence these have not been included in the addition process; hence k_a may be slightly low. The relative rate constants were determined by the equations:

$$k_a = \frac{12\,(\text{Ia} + \text{IIa})}{(\text{IX})}\,(\text{F}),\ k_{t_3} = \frac{6\,(\text{VI} + \text{VII})}{(\text{IX})}\,(\text{F}),\ k_{t_4} = \frac{4\,(\text{VIII})}{(\text{IX})}\,(\text{F})$$

where F = $(\text{Cyclohexane})_0/(\text{1-Butyne})_0$.

Equilibration of 1,2-*dichloro*-1-*butene.* A solution of 1·0 g Ia, 1·0 ml benzene (internal standard for GLC analysis), and 0·25 ml thiophenol in 50 ml hexane was illuminated under N_2 with a 275-w. sunlamp at a distance close enough to maintain reflux. Aliqouts (1 μl) were removed occasionally for GLC analysis to determine the ratio of Ia:IIa. An identical run was carried out with the IIa. The approach to equilibrium is shown in Table 3. Comparison of the peaks for Ia and IIa with that for benzene showed that little, if any, material was consumed.

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