Free-Radical Isomerization. I. A Novel Rearrangement of Vinyl Radicals

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Abstract: The free-radical addition of polyhalomethanes to terminal acetylenes has been studied. Besides the normal addition products, rearranged cyclic derivatives of 2,2-dichlorovinylcyclopentane were obtained in the addition of carbon tetrachloride and chloroform to terminal acetylenes of six carbon atoms or more. The formation of the cyclic products is attributed to the rearrrangement of the vinyl radical intermediates which undergo 1,5-internal hydrogen shift followed by internal cyclization. The temperature and solvent effects on the ratio of the rearranged to normal 1:1 adducts has been investigated, and the stereochemistry of the addition has been studied.

Intramolecular 1,5-hydrogen migration[1] in carbon radicals has been proposed in various polymerization[2] and thermal decomposition reactions.[3] Open-chain saturated alkyl radicals, unlike their cyclic analogs[4] which are prone to undergo transannular reactions,[5] or the corresponding oxygen[6] and nitrogen[7] radicals, do not readily abstract an internal 5-hydrogen atom.[8] However, we have found that open-chain vinyl radicals, due to their high reactivity, readily undergo internal 1,5-hydrogen shift in solution.

Although a large amount of quantitative data is now available for the reactions of alkyl radicals, comparatively little is known about the reactions of unsaturated alkyl radicals. We have studied the reactions and the reactivity of vinyl radicals generated by the addition of CCl_3 radicals to open-chain acetylenes. Specifically the free-radical additions of CCl_4 to hexyne-1, heptyne-1, and 6-methylheptyne-1 have been studied. The relative reactivity of the resulting secondary vinyl radicals for abstraction of internal primary, secondary, and tertiary hydrogen, in competition with chlorine transfer from CCl_4, has been determined. The effect of solvents on the extent of 1,5-hydrogen transfer relative to the bimolecular chlorine transfer from CCl_4 has also been studied.

Results

The Addition of Carbon Tetrachloride to Heptyne-1. The benzoyl peroxide initiated addition of CCl_4 to heptyne-1 proceeded readily, and the reaction products were distilled under vacuum. Three major products were isolated.

$$CH_3(CH_2)_4C{\equiv}CH + CCl_4 \xrightarrow{\text{peroxide}} \underset{\text{I}}{CH_3(CH_2)_4CCl{=}CHCCl_3} + \underset{\text{II}}{\text{(1-methyl-2-(2,2-dichlorovinyl)cyclopentane)}} + \underset{\text{III}}{CH_3(CH_2)_4CCl{=}CHCl}$$

The heptyne-1–carbon tetrachloride 1:1 normal addition product I, bp 90–92° (3 mm), was characterized by its elemental analysis and infrared and nmr spectra. The normal adduct I showed an olefinic infrared band at 1630 cm^{-1}. Its nmr spectrum contained a triplet at τ 3.5 (J = 0.7 cps, 1 H) and a multiplet at τ 7.3 (2 H) in addition to numerous peaks in the τ 8.3–9.3 region. The normal 1:1 adduct I readily eliminated one molecule of hydrogen chloride during vapor phase chromatography (22-ft 10% Carbowax 20 M on Chromosorb P at 180°) to yield a diene assigned the following structure: $CH_3(CH_2)_3CH{=}CClCH{=}CCl_2$. This diene exhibited an ultraviolet absorption band at $\lambda_{max}^{95\%\ EtOH}$ 252 mμ (log ϵ ~4.0). Its nmr spectrum contained a singlet at τ 3.7, a triplet at τ 3.95 (J = 7 cps), as well as multiple peaks in the τ 7.6–9.3 region.

Besides the normal addition product I, two lower boiling compounds were isolated. The more abundant product II, bp 77–80° (10.5 mm), consisted of two geometric isomers in about 1.7:1 ratio as determined by vapor phase chromatography. The nmr spectrum of the major isomer showed a doublet at τ 4.35 (J = 9.7 cps, 1.0 H), a multiplet at τ 7.2 (1.0 H), broad absorption in the τ 7.8–8.8 region (7.2 H), and another doublet at τ 9.2 (J = 6.5 cps, 2.9 H). The other isomer had a similar nmr spectrum but its low-field doublet appeared at τ 4.43 (J = 9.1 cps). The infrared spectrum of each isomer contained a sharp band at 1618 cm^{-1},[9] indicative of a —C=CCl_2 linkage.

The skeletal structure of the rearranged product II was confirmed by quantitative hydrogenation of the isomer mixture, in the presence of Raney nickel and alcoholic KOH,[10] to a mixture of *cis*- and *trans*-1-methyl-2-ethylcyclopentane, with the *cis* isomer predominating. The vpc retention times of these products as well as their mass spectra were identical with those of authentic samples.

The other major product III, bp 45–50° (8 mm), was shown to be the Cl_2 addition product of heptyne-1. Its

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nmr spectrum and vpc retention time were identical with those of an authentic sample. The chlorine adduct III is most likely a product of the ionic addition of molecular chlorine to the acetylene. Its yield is generally only 25–50% of the rearranged product II due to the probable loss of Cl_2 caused by sweeping the refluxing reaction mixture by a stream of nitrogen. This interpretation is in agreement with the finding that the apparent chain length decreased as the relative yield of the rearranged product II increased.

The ratio of the rearranged product II (R) over the normal adduct I (N) was determined at various concentrations of CCl_4. At constant heptyne concentration the ratio of N/R was found to increase linearily with the increase in [CCl_4] using 1-butanol as inert diluent (Figure 1).

The addition of CCl_4 to heptyne-1 was studied at three different temperatures, 61, 80, and 100°. The relative rates of 1,5-hydrogen shift to that of chlorine transfer corrected to 1 M concentrations of CCl_4 were determined. The activation energy for 1,5-hydrogen shift was found to be higher than the activation energy for chlorine transfer from carbon tetrachloride with $E_H - E_{Cl} = 2.7 \pm 0.5$ kcal/mole (Table I).

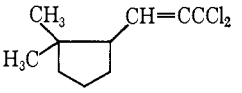
Table I. Summary of Data on the Selectivity of 1,5-Hydrogen Migration in the Addition of CCl_4 to Heptyne-1

Compound	k_R/k_N[a]	$(E_a)_R - (E_a)_N$	Log $\frac{A_R}{A_N}$	Rel react. per H
Hexyne-1	0.3	...	...	1
Heptyne-1	4.3	$+2.7 \pm 0.5$	2.4	22
6-Methyl-heptyne-1	65	-0.2 ± 0.2	1.4	650

[a] At 77°, in moles liter^{-1}.

When $BrCCl_3$ was substituted for CCl_4 in the addition to heptyne-1 no rearranged product was observed. The normal $BrCCl_3$–heptyne-1 1:1 adduct was the only major product isolated. Its infrared spectrum showed strong absorption at 6.17 μ, and the nmr spectrum contained an apparent singlet at τ 3.2 (1.0 H), a multiplet at τ 7.2 (2.0 H), and peaks at τ 8.2–8.9 as well as at τ 9.1 (3 H).

The Addition of CCl_4 to 6-Methylheptyne-1. The free-radical addition of CCl_4 to 6-methylheptyne-1 gave products similar to those obtained with heptyne-1. The ratio of the rearranged product over the normal adduct (R/N) was greater than 6:1 at 10 M concentration of carbon tetrachloride. The rearranged product, bp 86–89° (10 mm), consisted of a single isomer assigned the structure



Its nmr spectrum contained a doublet at τ 4.3 (J = 9.7 cps, 1 H) as well as two singlets at τ 9.0 (3 H) and 9.2 (3 H).

When bromotrichloromethane was substituted for carbon tetrachloride, 6-methylheptyne-1–$BrCCl_3$ 1:1 normal adduct was the only isolated product. The reaction product, bp 72–74° (0.02 mm), exhibited a strong infrared absorption band at 6.17 μ. Its nmr spectrum showed a triplet at τ 3.2 (J = 0.8 cps, 1 H), as well as a doublet at τ 9.1 ($J \cong 6$ cps, 6.0 H).

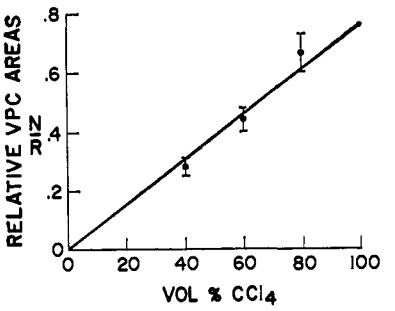


Figure 1. The variation in the ratio of N/R in the addition of CCl_4 to heptyne-1 (77°) at various carbon tetrachloride concentrations using t-butyl alcohol as an inert diluent.

The Addition of Carbon Tetrachloride to Hexyne-1. The addition of carbon tetrachloride to hexyne-1 proceeded to yield the hexyne-1–CCl_4 1:1 normal adduct as the major reaction product. The rearranged cyclic product appeared as a single isomer and its yield was estimated to be approximately 3% of the total adduct based on the vpc and nmr analysis of the crude reaction mixture. The nmr spectrum of the pure cyclic product (separated by vpc) showed the characteristic doublet at $\tau \sim 4.2$ (J = 8.8 cps). The normal 1:1 addition product, bp 64–65° (0.1 mm), displayed the characteristic infrared and nmr spectra. This compound loses one molecule of hydrogen chloride during vpc analysis to yield a diene assigned the structure $CH_3(CH_2)_2CH{=}CClCH{=}CCl_2$, based on its elemental analysis, infrared, ultraviolet, and nmr absorption spectra (see Experimental Section).

The Addition of Chloroform to Heptyne-1. The free-radical addition of chloroform to heptyne-1 proceeded to yield a mixture of products similar to those obtained from the addition of CCl_4 to heptyne-1. Besides the normal addition product, 1,1,1-trichlorooctene-2 and 1,2-dichloroheptene-1, the same cyclic products obtained with CCl_4, were isolated.

The ratio of R/N, calculated at 1 M concentration of chloroform, was 4.7 compared with a value of 4.3 obtained with CCl_4. The relative ratio of the rate constants for the hydrogen transfer from $HCCl_3$ and chlorine transfer from CCl_4 to the secondary vinylic radical ($k_{H\text{-}CCl_3}/k_{Cl\text{-}CCl_3}$) was 0.9.

The Addition of Chloroform to Hexyne-1. The benzoyl peroxide initiated addition of chloroform to hexyne-1 yielded one major fraction, bp 78–79° (7.5 mm). Our vpc analysis indicated the presence of two compounds, and it was possible to enrich fractions in each of these compounds by fractional distillation. Detailed analysis of the infrared and nmr spectra indicated these compounds to be the normal addition product, *cis*-1,1,1-trichloroheptene-2, and its allylic isomer, 1,1,3-trichloroheptene-1. The normal adduct could be readily isomerized to the more stable allylic isomer by heating at temperatures even below 100°, or by standing at room temperature in the presence of thionyl chloride. This isomerization could be easily followed by observing the nmr spectrum periodically, in particular, the appearance of a doublet at τ 4 at the expense of the 12-line ABX_2 pattern characteristic of the normal adduct. Isomerization by free-radical means, *i.e.*, per-

oxide or ultraviolet light, was not observed, nor was the isomerization detected to be reversible. Similar isomerizations were also observed with other acetylene–$CHCl_3$ adducts (Table II).

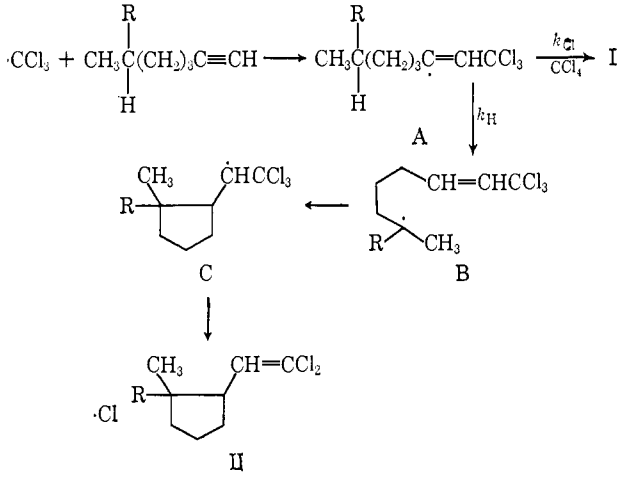
Table II. Physical Data for Hexyne–$CHCl_3$ Adducts

	(X) $C_3H_7CH_2$ CCl_3 $C=C$ H_B H_A	(X) $C_3H_7CH_2$ CCl_2 Cl $C-C$ H_B H_A
Nmr		
τ_A	3.73[a]	4.0
τ_B	4.40	5.4
τ_X	7.46	...
J_{AB}	11.46 cps	9.7 cps
J_{AX}	−1.92 cps	...
J_{BX}	7.70 cps	6.5 cps
Infrared		
C=C	6.08 μ	6.17 μ
Vpc:[b]		
Ret time	32 min	38 min

[a] Chemical shifts and coupling constants for the ABC_2 spectrum were calculated using the LAOCOON program. Probable errors are ±0.05 cps. [b] 4-ft 10% Apiezon L on Chromosorb W at 80°, with helium flow of 150 cc/min and injection port at 160°.

Discussion

The normal 1:1 addition products obtained from the free-radical addition of CCl_4 or $HCCl_3$ to hexyne-1, heptyne-1, and 6-methylheptyne-1 can be attributed to a chain reaction involving the addition of a $\cdot CCl_3$ radical to the acetylene, followed by chlorine transfer from CCl_4 or hydrogen transfer from $HCCl_3$ to the resulting radical intermediate as has been discussed elsewhere.[11] The formation of the unusual cyclic product, however, can be explained by the following sequence of reactions.



This mechanism displays three reaction steps involving free radicals: (1) intramolecular 1,5-hydrogen abstraction, (2) internal cyclization by addition to a double bond,[12] and (3) halogen elimination from a β-halo radical.[13] This halogen elimination is considerably faster than chlorine transfer from CCl_4 in our system.

The cyclization of radical B to a five-membered ring is much faster than chlorine transfer from carbon tetrachloride as evidenced by the absence of the γ-chloro isomer (1,1,1,7-tetrachlorooctene-2). This is in accord with the reported result which shows that the free-radical addition of CCl_4 to diallyl ether gives a tetrahydropyran derivative at the expense of the corresponding 1:1 normal addition product.[14]

Even the presence of thiols, with their high hydrogen transfer constants,[15] did not prevent extensive cyclization of the radical derived from ethyl diallylacetate.[16]

An alternate mechanism involving direct insertion by a carbene derived from the intermediate vinyl radical

$$C_5H_{11}\dot{C}{=}CHCCl_3 \xrightarrow{-Cl\cdot} C_5H_{11}\ddot{C}CH{=}CCl_2$$

seems extremely unlikely in view of the high selectivity between primary, secondary, and tertiary hydrogens observed, as well as the preference for five-membered-ring formation which is inconsistent with a carbene intermediate.[17]

The interesting feature of our results is that the vinyl radical intermediate resulting from the addition of trichloromethyl radical to terminal acetylenes can undergo internal 1,5-hydrogen shift while the corresponding secondary alkyl radicals fail to do so.[18] This can be attributed to the high reactivity of the vinyl radical, which is suggested by the relatively high vinylic C–H bond dissociation energy. The activation energy difference for 1,5-hydrogen shift to the vinyl radical derived from heptyne-1 and that of chlorine transfer from CCl_4 ($E_H - E_{Cl}$) is 2.7 ± 0.5 kcal/mole. This difference should be greater for the corresponding secondary alkyl radicals, and hence the rate of chlorine transfer would greatly exceed that of the internal 1,5-hydrogen shift. Although our data point out that secondary vinyl radicals are more reactive than the corresponding secondary alkyl radicals, they are also more reactive than primary alkyl radicals. Comparison of the relative ratio of 1,5-hydrogen shift to chlorine transfer for the secondary vinyl radical with the corresponding ratio reported for the primary alkyl radical $CCl_3(CH_2)_5CH_2\cdot$, corrected to the same temperature, leads to a value of $(k_H/k_{Cl})_{vinyl}/(k_H/k_{Cl})_{primary} \cong 560$.[19] This indeed is in accord with the postulated high reactivity of vinyl radicals.

The selectivity of the vinyl radical (B) for intramolecular 1,5 abstraction of a primary, secondary, or tertiary hydrogen is of the order 1:22:650. Such high selectivity, however, should not be expected in bimolecular hydrogen abstraction processes. The carbon–hydrogen abstraction in bimolecular reactions follows a path requiring the least activation energy in which the ap-

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(19) In the above calculation it is assumed that a β-CCl_3 group affects both the hydrogen and chlorine transfer to the same extent.

proaching radical lies linear with the C–H bond under attack.[20] Intramolecular 1,5-hydrogen shift, however, involves a cyclic transition state in which the C–H–C angle is less than 180°, and hence necessitates a relatively high activation energy. This explanation is in accord with the finding that 1,5-hydrogen abstractions by alkoxy radicals exhibit greater selectivity than bimolecular hydrogen abstraction by the same radical.[21]

Stereochemistry of Addition. The stereochemistry of free-radical additions to acetylenes has received considerable interest lately, especially as related to the properties of the intermediate vinyl radicals. In our studies of the addition of CCl_4 and $BrCCl_3$ to terminal acetylenes, essentially one major normal adduct was isolated. We believe this isomer to be the *trans* addition product on the basis of its low allylic coupling constant (0.7 cps), which agrees well with the *trans* allylic coupling constants observed in various 2-substituted propenes.[22]

The chloroform reactions yielded predominantly one normal adduct which was contaminated with 10–20% of another isomer.[23] The major adduct could be readily isomerized, both thermally and ionically, to the minor isomer, which was shown to be the allylic rearrangement product.[24]

$$RC(H)=CHCCl_3 \xrightarrow{\Delta} RCH(Cl)CH=CCl_2$$

We attribute the appearance of the rearranged vinylidene isomer to thermal and ionic background during the reaction itself and during distillation of the reaction mixture. Reverse isomerization to the trichloromethyl olefin was not observed.

The major adduct is presumed to be the *cis* product (*trans* addition of $CHCl_3$) on the basis of the coupling constant between the two vinyl protons (11.46 cps) which agrees quite favorably with the *cis* couplings observed (10–12 cps) in a variety of carbon-[25a] and sulfur-substituted[25] olefins.

Since one would not expect the observed *cis* product (*trans* addition) to be the thermodynamically favored isomer, its formation must be the result of kinetic control.

The preference for *trans* addition of polyhalomethanes to terminal acetylenes agrees well with the stereochemistry observed in the addition of other radicals to acetylenes.[26]

In view of the facile interconversion of isomeric vinyl radicals and the importance of steric control in the hydrogen-transfer process,[27] exclusive transfer of hydrogen *trans* to the bulky trichloromethyl group is not unexpected.

$$R\text{–}C(\cdot)=C(H)\text{–}CCl_3 \rightleftharpoons R\text{–}C(\cdot)=C(H)\text{–}CCl_2$$

Effects of Solvents on the Ratio of Internal Hydrogen Abstraction to Chlorine Transfer from CCl_4. The competition between the intramolecular 1,5-hydrogen shift and the bimolecular chlorine transfer from carbon tetrachloride was found to be influenced by solvents (Table III). The influence on these two processes did not follow any simple solvent polarity. Benzene showed the highest effect and it favored internal hydrogen abstraction at the expense of the chlorine transfer.

Table III. Effect of Solvents on the Ratio N/R with Heptyne-1 in 75% CCl_4 at 61°

Solvent	N/R
25% inert (calculated)	1.72
25% *t*-BuOH	1.75
45% tetrachloroethylene	1.57
25% acetonitrile	1.16
25% benzene	0.95

We attribute this effect to complexing of the vinyl radical intermediate with the π electrons of the solvents. The influence of complexing solvents usually favors the process with the lowest activation energy.[28] However, our results indicate that the internal hydrogen abstraction process, which is the reaction of higher activation energy, is actually favored. Examination of Figure 2 illustrates that the dilution of CCl_4 with benzene leads to a drastic initial effect which then levels off at about 60% benzene. The curved portion of the plot in Figure 2 is due to the varying degree of complexing at different benzene concentrations, while the linear portions merely represent a dilution effect on the fully complexed radicals. Extrapolation of the linear portion of the plot to 100% CCl_4 leads to a value of k_H/k_{Cl} for the complexed vinyl radical approximately 2.5 times greater than that for the noncomplexed vinyl radical. The most plausible explanation for such a solvent effect is that complexing favors the unimolecular reaction relative to the bimolecular chlorine transfer process.

Experimental Section

Nuclear magnetic resonance spectra were determined on a Varian A-60 spectrometer. Chemical shifts are reported in τ with $(CH_3)_4Si$ as external standard. The ultraviolet absorption spectra were carried out using a Cary Model 14 spectrophotometer. Infrared spectra were determined on a Perkin-Elmer Model 237 spectrophotometer.

Materials. Heptyne-1 and hexyne-1 were commercially available chemicals of over 98% purity and were used as such.

6-Methylheptyne-1 was prepared by the following procedure. The free-radical addition of HBr to 4-methylpentene-1, initiated by ultraviolet light at −40°, yielded 1-bromo-4-methylpentane, bp 146°. An ether solution of 1-bromo-4-methylpentane was refluxed for 72 hr with lithium acetylide–ethylenediamine complex to yield 6-methylheptyne-1 (30% yield), bp 118°.

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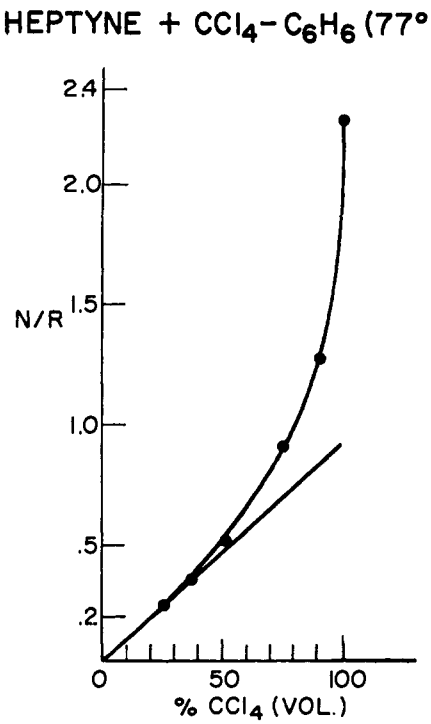

Figure 2. The variation in the ratio of N/R in the addition of CCl_4 to heptyne-1 (77°) at various benzene concentrations in carbon tetrachloride.

The Addition of Carbon Tetrachloride to Terminal Acetylenes. General Procedure. A 0.3 M solution of the acetylene in CCl_4 (or chloroform) was refluxed for 24 hr under a stream of nitrogen and in the presence of 0.03 M benzoyl peroxide. The reaction mixture was cooled, extracted with 10% sodium carbonate solution, dried over anhydrous sodium sulfate, and evaporated. The residue was distilled under vacuum, and the different fractions were characterized by their infrared and nmr spectra.

The product and solvent effect studies were carried out in a constant-temperature bath. The residues obtained after evaporation of the solvent were analyzed by two methods: (1) vapor phase chromatography at 180° using a 22-ft column of 10% Carbowax (20 M) on Chromosorb P. The normal polyhalomethane–acetylene 1:1 addition products lost one molecule of HCl on the column yielding a diene which was characterized by its ultraviolet and nmr spectra. In general, the weight per cent of the normal and the rearranged products were calculated from their corresponding vpc peak areas, and the peak areas were calibrated using mixtures of known composition. All the experimental runs were carried out in duplicate and each run was analyzed in triplicate. (2) Nuclear magnetic resonance spectra of the crude reaction product. The ratio of the normal to the rearranged products was determined from the peak areas of the vinylic hydrogens characteristic of these products. In general there was a fairly good agreement, within ±10%, between the results obtained by either method 1 or 2.

The Addition of CCl_4 to Heptyne-1. Heptyne-1 (0.3 mole) was dissolved in CCl_4 (1500 cc) and benzoyl peroxide (4 g) was added. The solution was refluxed under a dry stream of nitrogen for 24 hr. Distillation of the crude reaction mixture yielded three major products.

a. A colorless liquid (3.0 g, 6%), bp 45–50° (8 mm), was shown to be 1,2-dichloroheptene-1; infrared (CCl_4): 3.22 and 6.31 μ; nmr: τ 4.0 (triplet, $J \cong 0.7$ cps, 1 H), τ 7.5 (multiplet, 2.0 H), and τ 8.3–9.3 (8.8 H). *Anal.* Calcd for $C_7H_{12}Cl_2$: C, 50.30; H, 7.24; mol wt, 166. Found: C, 50.28; H, 7.26; mol wt, 166.

b. A colorless oil (10.7 g, 20%), bp 77–80° (10.5 mm), was shown to be a mixture of the *cis* and *trans* isomers of 1-(2,2-dichlorovinyl)-2-methylcyclopentane; infrared (CCl_4): 1618 cm^{-1}; nmr of major isomer: τ 4.35 (doublet, J = 9.7 cps, 1.0 H), τ 7.2 (multiplet, 1.0 H), τ 7.8–8.8 (multiplet, 7.2 H), and τ 9.2 (doublet, J = 6.5 cps, 2.9 H). *Anal.* Calcd for $C_8H_{12}Cl_2$: C, 53.63; H, 6.76; Cl, 39.6; mol wt, 178. Found: C, 53.33; H, 6.87; Cl, 39.1; mol wt, 178.

c. A colorless oil (30 g, 40%), bp 90–92° (3 mm), was assigned the structure 1,1,1,3-tetrachlorooctene-2 (heptyne-1–CCl_4, 1:1 adduct); infrared (CCl_4): 1630 cm^{-1}; nmr: τ 3.5 (triplet), J = 0.7 cps, 1 H), τ 7.3 (multiplet, 2 H), and τ 8.3–9.3 (multiplet). *Anal.* Calcd for $C_8H_{12}Cl_4$: C, 38.41; H, 4.84; Cl, 56.75. Found: C, 39.81; H, 4.94; Cl, 55.2. The poor analysis of this compound was due to traces of phenyl benzoate which could not be removed even after repeated distillations. *Anal.* Calcd for 3% phenyl benzoate impurity: C, 39.62; H, 4.85; Cl, 55.05. This compound lost one molecule of HCl during vpc analysis and yielded a diene which was assigned the structure $CH_3(CH_2)_3CH{=}CCl\text{-}CH{=}CCl_2$. *Anal.* Calcd for $C_8H_{11}Cl_3$: C, 44.97; H, 5.19. Found: C, 45.35; H, 5.42. The ultraviolet spectrum exhibited λ_{max} 252 mμ (log ϵ ~4.0) in 95% ethanol; nmr: τ 3.7 (singlet), τ 3.95 (triplet, J = 7 cps), and τ 7.6–9.3 (multiplet).

The Hydrogenation of 1-(2,2-Dichlorovinyl)-2-methylcyclopentane (The Rearranged Product). Fraction b (2 g) was dissolved in 10% alcoholic KOH (40 cc); Raney nickel (0.2 g) was added, and the reaction mixture was hydrogenated at room temperature for 18 hr under 60-psi hydrogen pressure. The hydrogenated reaction mixture was filtered, diluted with water, extracted with ether, dried, and evaporated. The residue (≈1.2 g) was shown to be a mixture of *cis*- and *trans*-1-ethyl-2-methylcyclopentane (ratio 1.3:1). The hydrogenated products were identical with authentic samples of *cis*- and *trans*-1-ethyl-2-methylcyclopentane based on vpc retention times and mass spectra.

The Addition of Carbon Tetrachloride to 6-Methylheptyne-1. 6-Methylheptyne-1 (14 g), CCl_4 (350 cc), and benzoyl peroxide (1.0 g) were refluxed for 22 hr. The vpc analysis and the nmr spectrum of the crude reaction mixture indicated that the ratio of the rearranged product to the normal addition product was ~6:1. Distillation of the reaction mixture yielded: (a) colorless liquid (1.4 g), bp 73–83° (10 mm); (b) colorless liquid (6 g, 24%), bp 86–89° (10 mm). The vpc analysis of this compound showed only one isomer and was assigned the structure 1-(2,2-dichlorovinyl)-2,2-dimethylcyclopentane; nmr: τ 4.3 (doublet, J = 9.7 cps, 1 H), τ 7.3–8.8 (multiplet), τ 9.0 (singlet, 3 H), and τ 9.2 (singlet, 3H). *Anal.* Calcd for $C_9H_{14}Cl_2$: C, 55.95; H, 7.31; Cl, 36.7. Found: C, 55.90; H, 7.32; Cl, 36.6. (c) Colorless oil (1.8 g, 6%), bp 73–80° (0.06 mm). It had an infrared and nmr spectrum which was expected from a 6-methylheptyne-1–CCl_4, 1:1 normal addition product. (d) Tarry residue (4.5 g).

The Addition of Carbon Tetrachloride to Hexyne-1. Hexyne-1 (36.9 g), benzoyl peroxide (4.5 g), and CCl_4 (1500 cc) were refluxed under nitrogen for 22 hr. The vpc analysis of the crude reaction mixture as well as its nmr spectrum revealed that the ratio of the rearranged product to the normal addition product was ≃0.03. Distillation of the reaction mixture yielded (a) liquid (1 g), bp 40–60° (0.1 mm). This fraction yielded one isomer when purified by vpc (which was assigned the structure 2,2-dichlorovinylcyclopentane); nmr: τ ~4.2 (doublet, $J \approx$ 8.8 cps, 1 H). *Anal.* Calcd for $C_7H_{10}Cl_2$: C, 50.91; H, 6.11. Found: C, 51.50; H, 6.18. (b) Colorless oil (41.6 g, 40%), bp 64–65° (0.1 mm). The infrared spectrum showed 3.24 and 6.12 μ. Its nmr spectrum indicated essentially one isomer which had a singlet at τ 3.4 (1 H), multiplet at τ 7.2 (2 H), and numerous peaks at τ 8.2–9.2 (7.4 H). This compound was assigned the structure 1,1,1,3-tetrachloroheptene-2. *Anal.* Calcd for $C_7H_{10}Cl_4$: C, 35.61; H, 4.27. Found: C, 36.28; H, 4.43 (calculated for 1% phenyl benzoate impurity: C, 36.04; H, 4.33).

The Addition of Chloroform to Heptyne-1. Heptyne-1 (48 g), benzoyl peroxide (7.5 g), and chloroform (1500 cc) were refluxed for 114 hr. Distillation of the crude reaction mixture yielded (a) liquid (≃1.5 g), bp 45–55° (7 mm). This fraction was shown to be mainly 1,2-dichloroheptene-1. (b) Liquid (≃3.2 g, 4%), bp 68–70° (7 mm). This fraction was shown to be a mixture of *cis*- and *trans*-1-(2,2-dichlorovinyl)-2-methylcyclopentane based on the vpc analysis and infrared and nmr spectra. (c) Colorless liquid (14.5 g, 14%), bp 62° (0.1 mm). This compound was shown to be mainly 1,1,1-trichlorooctene-2; infrared (CCl_4): 6.18 μ. *Anal.* Calcd for $C_8H_{13}Cl_3$: C, 44.56; H, 6.08. Found: C, 44.11; H, 6.04.

The Addition of $CHCl_3$ to Hexyne-1. Hexyne-1 (71.5 g), benzoyl peroxide (10 g), and CCl_4 (1000 ml) were refluxed under nitrogen for 90 hr. Distillation yielded one major fraction, bp 78–79° (7.5 mm), 37.5 g (22%). Analysis of the nmr and infrared spectra indicated the presence of two major compounds, the normal addition product, *cis*-1,1,1-trichloroheptene-2, along with 10–20% of its allylic isomer, 1,1,3-trichloroheptene-1. The existence of minor amounts of a third isomer cannot be excluded; infrared (CCl_4):

6.08 (1,1,1-trichloroheptene-2) and 6.17 μ (1,1,3-trichloroheptene-1). The nmr spectrum showed a complicated pattern of absorption in the τ 3.6–4.7 region, which was shown to result from a 12-line ABX_2 system (1,1,1-trichloroheptene-2) and a doublet (1,1,3-trichloroheptene-1). The isomerization of 1,1,1-trichloroheptene-2 to its allylic isomer was easily followed by means of the nmr spectrum: 1,1,1-trichloroheptene-2: τ_A 3.73, τ_B 4.40, J_{AB} = 11.46 cps, J_{AX_2} = 1.92 cps; 1,1,3-trichloroheptene-2: τ_A 4.0, τ_B 5.4, J_{AB} = 9.7 cps.

Isomerization was accomplished by heating a sealed nmr tube containing the product in an oven maintained at 95° for 6 hr or more. The addition of thionyl chloride to the product catalyzed isomerization at room temperature.

The Addition of Bromotrichloromethane to Heptyne-1. Heptyne-1 (0.1 mole) and $BrCCl_3$ (0.4 mole) were transferred into a quartz tube, flushed with nitrogen, and sealed under vacuum. The tube was irradiated for 6 hr with ultraviolet light from a 200-w Hanovia lamp. The reaction mixture was distilled to yield one major product, bp 72–74° (0.02 mm). The infrared and nmr spectra of the distillate indicated that it was the heptyne-1–$BrCCl_3$ 1:1 normal adduct. The infrared spectrum showed bands at 6.17 (C=C) and 7.22 μ (*gem*-dimethyl); nmr: triplet at τ 3.2 (J = 0.8 cps, 1.0 H), multiplet at τ 7.2 (2.0 H), and doublet at τ 9.1 ($J \approx 6$ cps, 6.0 H).

The addition product obtained from the addition of $BrCCl_3$ to 6-methylheptyne-1, bp 72–74° (0.02 mm), was also found to be the normal 1:1 adduct.

A Comparison of Allylic and Propargylic Radicals

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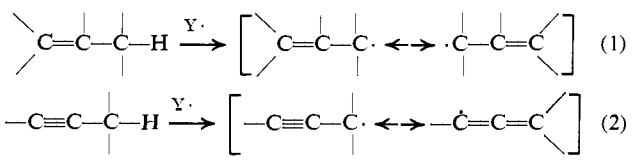
Abstract: Through a study of the thermal, homolytic concerted decompositions of the β,γ-olefinic and β,γ-acetylenic peresters Ia–f, activation parameters for processes generating allylic and propargylic radicals have been determined. These activation parameters establish that the 2-buten-1-yl radical (IIa) is about 4 kcal/mole more stable than the 2-butyn-1-yl radical (IIb), but that the additional stability of the allylic radical is achieved only through the imposition of rotational restrictions not imposed upon the propargyl radical. Radical stabilization through delocalization in a propargyl radical requires no rotational restrictions as a consequence of the cylindrical symmetry of the triple bond. The γ-phenyl group of the 3-phenyl-2-propen-1-yl radical (IId) increases the stability of the radical by extending the conjugated system, whereas the γ-phenyl group of the 3-phenyl-2-propyn-1-yl radical (IIe) confers very little added stability to the propargyl radical, suggesting that the delocalization of the free electron does not extend into the benzene ring.

The formation of allylic free radicals through hydrogen abstraction is the first step in a number of synthetically useful reactions, such as allylic halogenation with N-bromosuccinimide[3] and *t*-butyl hypochlorite.[4] Analogous reactions, utilizing acetylenic substrates,[5,6] though less frequently employed, also reflect the possibility of selective hydrogen abstraction at a propargylic position. The origin of the greater ease of abstraction



(1)

(2)

of an allylic or propargylic atom when compared to hydrogen abstraction from carbon atoms not adjacent to multiple bonds is obviously the formation of resonance-stabilized radicals, the contributing canonical forms for which are depicted in eq 1 and 2.

It is important to recognize, however, that there are some significant differences between allylic and propargylic radicals and consequently also between processes which generate them. For instance, the two contributing canonical forms of the allylic radical are structurally similar and therefore of very similar energies, whereas the two contributing structures of the propargyl radical, one acetylenic and one allenic, are not of equal energies. Hence, it would be anticipated that resonance stabilization of an allylic radical would be greater than for a propargylic radical. Bond energy data tend to support this contention. Although there is rather wide variation in bond disssociation values reported for allylic and propargylic bonds when measured by different methods, allylic bond dissociation energies are generally about 3–4 kcal/mole less than propargylic bond dissociation energies when measured by the same method in analogous compounds.[7–10] However, since the formation of a resonance-stabilized allylic radical requires overlap of the three p orbitals involved in the delocalized three-electron system, rotation of the bond between the allylic carbon atom and the double bond is necessarily restricted in the radical. There are no such restrictions in the propargyl radical, since the cylindrical symmetry of a triple bond permits overlap of the p orbital on the propargylic carbon atom in any rotational state. Thus an allyl radical is more stable than an analogous propargyl radical, but its added stability is purchased at the price of a loss in rotational freedom. Hence, one would be led to expect that a process leading to an allylic radical would have a lower enthalpy of

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