Vinyl Radicals. IV.[1] The Stereochemistry of the Free-Radical Addition of Chloroform to Alkylacetylenes

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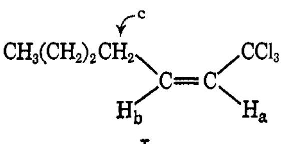
Abstract: The benzoyl peroxide catalyzed addition of chloroform to 1-hexyne gives a complex mixture consisting of *cis-* and *trans*-1,1,1-trichloroheptenes-2 and the allylic rearrangement product, 1,1,3-trichloroheptene-1. *cis-* and *trans*-1,1,1-trichloroheptenes-2 are formed in 82:18 proportions under conditions of kinetic control. Similar stereochemical results are obtained in the addition of chloroform to 1-octyne. These observations are analyzed in terms of isomeric vinyl radical intermediates which interconvert rapidly with respect to subsequent reactions. Particular attention is given to a discussion of the isomeric composition of a product mixture derived from rapidly equilibrating vinyl radicals.

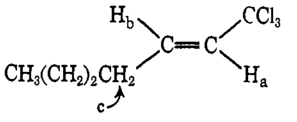
Several recent studies have probed the characteristic behavior of vinyl free radicals. One fruitful approach to these radicals involves the homolysis of α,β-unsaturated peresters.[1,2] An alternative method of generating these radicals employs the addition of a free radical to an acetylene. We have previously reported the kinetically controlled stereochemistry of the radical addition of thioacetic acid to 1-hexyne.[3] The present paper describes studies of the radical-catalyzed addition of chloroform to alkylacetylenes. Chloroform was chosen as an addendum of low chain transfer ability, representative of one of the limiting cases of competition between isomerization and capture of the intermediate vinyl radicals. The free-radical addition of chloroform to alkylacetylenes was recently described by Heiba and Dessau.[4] In general, our separate studies have focused on different aspects of the reaction.

Results

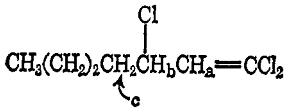
The benzoyl peroxide initiated addition of chloroform to 1-hexyne in a nitrogen atmosphere at 61° gives a mixture of trichloroheptenes in yields as high as 85%. The product mixture isolated by distillation after 5-hr reaction time shows 1640 and 1650 cm^{-1} olefinic absorption in the infrared spectrum. As described below, this material was shown to be a *cis–trans* mixture of 1,1,1-trichloroheptene-2 ($I_{c,t}$). Very long reaction times (>200 hr) give a product with strong 1620-cm^{-1} activity, but relatively free of 1640- and 1650-cm^{-1} absorptions. This material was purified to give only 1620-cm^{-1} absorption and characterized as 1,1,3-trichloroheptene-1 (II). An intermediate reaction time (120 hr) gives a mixture with infrared absorptions at 1640, 1650, and 1620 cm^{-1} ($I_{c,t}$ + II). Each mixture of reaction products analyzes as $C_7H_{11}Cl_3$. These infrared observations suggest the initial formation of a mixture of two trichloroheptenes ($I_{c,t}$) and subsequent rearrangement of these to a third trichloroheptene (II) under the reaction conditions.



I_c



I_t



$$CH_3(CH_2)_2CH_2\overset{Cl}{C}H_bCH_a{=}CCl_2$$

II

The 1640- and 1650-cm^{-1} infrared absorptions of the reaction mixture from short reaction times ($I_{c,t}$) indicate a mixture of the expected chloroform–hexyne adducts. The nmr spectrum of this mixture shows a relative ratio of 2:2:7 for olefinic, allylic, and alkyl protons. The spectrum is complicated, but can be interpreted in terms of a mixture of isomeric materials, I_c and I_t, in which the *cis* isomer (I_c) predominates. The spectrum of compound I_c could be deduced from the spectrum of the mixture and shows single olefinic protons at τ 3.72 (H_a) and 4.42 (H_b); J_{ab} = 11.5 Hz. Both olefinic protons are further coupled to an allylic methylene group ($2H_c$); J_{ac} = 2.0 Hz and J_{bc} = 7.5 Hz. The remainder of the nmr spectrum of the mixture was assigned as a complex second-order pattern due to the *trans* isomer, I_t.

The *cis–trans* mixture ($I_{c,t}$) could not be fractionated by distillation or vapor phase or thin layer chromatography. The *trans* isomer (I_t) was synthesized[5–8] for comparison by the alkaline dehydrobromination of the adduct of bromotrichloromethane and hexene-1. The material prepared by this route gives infrared absorption at 1650 cm^{-1} and analyzes as $C_7H_{11}Cl_3$. The nmr spectrum shows a complex multiplet centered at τ 3.82 (H_a,H_b), a multiplet at 7.84 ($2H_c$), and alkyl absorption. This spectrum of I_t was identical with that deduced by interpretation of the spectrum of the *cis–trans* reaction mixture ($I_{c,t}$). Computer analysis[9] of the second-order vinyl region of the spectrum of I_t gave the following parameters: τ 3.90 (H_a), 3.77 (H_b), J_{ab} =

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[1] Part III: R. M. Fantazier and J. A. Kampmeier, *J. Amer. Chem. Soc.*, 88, 5219 (1966).

[2] L. A. Singer and N. P. Kong, *Tetrahedron Lett.*, 643 (1967); *J. Amer. Chem. Soc.*, 89, 6805 (1967).

[3] J. A. Kampmeier and G. Chen, *ibid.*, 87, 2608 (1965).

[4] E. I. Heiba and R. M. Dessau, *ibid.*, 89, 3772 (1967).

[5] A. N. Nesmeyanov, R. K. Freidlina, and L. I. Zakharkin, *Quart. Rev.* (London), 10, 330 (1956).

[6] M. S. Kharasch, J. J. Jerome, and W. H. Urry, *J. Org. Chem.*, 15, 966 (1950).

[7] H. Goldwhite, M. S. Gibson, and C. Harris, *Tetrahedron*, 20, 1613 (1964).

[8] E. C. Kooyman and W. M. Wagner, *Rec. Trav. Chim. Pays-Bas*, 77, 923 (1958).

[9] LAOCOON II, S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 41, 3863 (1964), revised to fit an IBM 7074 computer by A. H. Turner.

16.4 Hz; 7.85 ($2H_c$), $J_{ac} = 2.0$ Hz and $J_{bc} = 7.5$ Hz. The relative magnitudes of the olefinic coupling constants,[10] J_{ab}, allow the *cis* and *trans* assignments to I_c and I_t, respectively. This assignment is confirmed by the independent synthesis of I_t.

Further confirmation of the structural assignments was obtained by ozonolysis. The *cis–trans* reaction product ($I_{c,t}$) and the pure *trans* material (I_t) both gave good yields (>50%) of chloral and valeraldehyde when degraded with ozone at −78° in the presence of tetracyanoethylene.[11] Chloral and valeraldehyde were characterized as 2,4-dinitrophenylhydrazine derivatives; yields of the aldehydes were determined by vpc. Other aldehydes and/or ketones were not detected. A mixture of products was obtained in >95% total yield when the ozonolysis was conducted in the absence of tetracyanoethylene. These products were characterized as ozonides by ir and nmr spectra. The mixtures of ozonides from $I_{c,t}$ and from pure I_t gave ir and nmr spectra which differed only in the relative intensities of the absorptions. This is in accord with recent observations[12] that *cis* and *trans* olefins give different mixtures of isomeric ozonides.

The ir absorption of II at 1620 cm^{-1} indicates[9,13] a *gem*-dichlorovinyl structure. The nmr spectrum of II shows absorption at τ 4.05 (doublet, H_a, $J_{ab} = 9.8$ Hz), at 5.40 (multiplet, H_b, $J_{bc} = 6.6$ Hz), and aliphatic absorption. II is inert to ozone at −78°, as observed[8] for other dichlorovinyl systems. The *cis–trans* mixture ($I_{c,t}$) and the *trans* isomer (I_t) were shown to rearrange to the allylic chloride II under a variety of conditions, including refluxing chloroform. This rearrangement has been previously observed[4,5] for trichloroolefins of structure I. In conclusion, therefore, the free-radical addition of chloroform to hexyne-1 gives a mixture of *cis*- and *trans*-1,1,1-trichloroheptenes-2 ($I_{c,t}$) with the *cis* isomer as the major product. Both isomers rearrange under the reaction conditions to 1,1,3-trichloroheptene-1 (II).

As mentioned previously, the *cis–trans* mixture of 1,1,1-trichloroheptenes could not be separated by vapor phase chromatography; either decomposition or rearrangement to II occurred under all conditions tried. It was possible, however, to determine the *cis/trans* product ratio by careful analysis and integration of the nmr spectra of the product mixtures. Absorptions due to the rearrangement product II do not interfere with this determination. The *cis/trans* adduct ratio was found to be 82 ± 3/18 and to be independent of the reaction time. Appropriate control experiments showed that this isomer ratio is kinetically determined. Mixtures of I_c and I_t varying in composition from 100% *trans* to 80% *cis*, 20% *trans* were prepared by mixing known weights of the $I_{c,t}$ reaction mixture and pure I_t prepared by the dehydrobromination route. These mixtures were refluxed in chloroform with benzoyl peroxide until 80–90% of the original 1,1,1-trichloroheptenes had rearranged to 1,1,3-trichloroheptene-1. The I_c/I_t ratio determined by nmr remained in agreement with the known weight composition of the mixtures. Thus, this isomerization effects the absolute yields of I_c and I_t, but does not alter the ratio of the two. We were not able to determine the thermodynamic ratio of I_c/I_t; all attempts at *cis–trans* equilibration gave rearrangement to II. We were able to show that *cis–trans* isomerization is not important under the reaction conditions by the following experiment. Pure *trans* isomer was added to a reaction mixture consisting of chloroform, 1-octyne, and benzoyl peroxide. Work-up gave recovered *trans*-1,1,1-trichloroheptene-2 with no detectable trace of the *cis* isomer, while *cis*- and *trans*-1,1,1-trichlorononenes-2 (chloroform–octyne adducts) were formed in an 82:18 isomer ratio.

The temperature dependence of the stereochemistry of the addition of chloroform to hexyne was studied briefly. Attempts to use benzophenone triplet to initiate the addition were unsuccessful; irradiation of degassed solutions of benzophenone, chloroform, and 1-hexyne at room temperature did not lead to significant yields of chloroform–hexyne adducts. It was possible, however, to use the benzophenone-sensitized decomposition of benzyl peroxide[14] as an initiator system. Moderate yields of the normal adducts ($I_{c,t}$) were obtained by irradiation of solutions of 1-hexyne, chloroform, benzoyl peroxide, and benzophenone at 0 and 17°. The observed *cis/trans* adduct ratio was 80 ± 3/20 and was independent of irradiation time. Further support for kinetic control was provided by the observation that authentic *trans* adduct I_t was not isomerized by irradiation in the presence of chloroform, benzoyl peroxide, and benzophenone. The *cis–trans* adduct composition at 0 and 17° is within experimental error of that observed in the thermal reaction at 61°.

The results of chloroform–octyne reactions are similar to those described for hexyne with the added complication of the intramolecular abstraction–cyclization reaction discovered by Heiba and Dessau.[4] Thus, the mixture of noncyclic adducts consists of *cis*- and *trans*-1,1,1-trichlorononenes-2 and the corresponding allylic isomer, 1,1,3-trichlorononene-1. The *cis/trans* adduct ratio is 82 ± 3/18 and is kinetically controlled. These normal adducts were characterized and determined by methods analogous to those described for the hexyne studies.

Other products, derived from the abstraction–cyclization route, were observed. The major component of this group of products is assigned as a mixture of *cis*- and *trans*-1-ethyl-2-(β,β-dichlorovinyl)cyclopentanes (III). The isomers were separable by vpc and analyzed as $C_9H_{14}Cl_2$. The main spectral properties of the two isomers are identical with those described by Heiba and Dessau for *cis*- and *trans*-1-methyl-2-(β,β-dichlorovinyl)cyclopentanes; differences were observed, as expected, in the aliphatic region of the nmr spectrum. A minor component of this group of products was tentatively assigned as 1-ethyl-2-trichloromethylcyclohexane (IV, presumably a mixture of isomers). This material analyzes as $C_9H_{15}Cl_3$, shows strong infrared absorption at 765, 750, and 695 cm^{-1} suggesting[15] a trichloromethyl group and lacks olefinic absorption. The nmr spectrum shows no absorption below τ 7.6 indicating the absence of olefinic protons and protons on carbon bear-

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(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press, Ltd., London, 1959.

(11) R. Criegee and P. Günther, *Ber.*, **96**, 1564 (1963).

(12) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **88**, 3143 (1966).

(13) D. G. Kundiger and H. Pledger, Jr., *ibid.*, 78, 6098 (1956).

(14) C. Walling and M. J. Gibian, *ibid.*, 87, 3413 (1965).

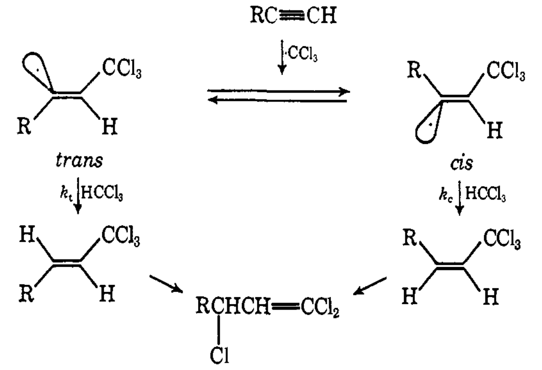
(15) E. C. Kooyman and E. Farenhorst, *Rec. Trav. Chim. Pays-Bas*, 70, 867 (1951).

ing chlorine; a triplet at τ 9.1 (J = 7 Hz, 3 H) indicates an ethyl group. The benzoyl peroxide initiated reaction of chloroform with 1-ethylcyclohexene was studied as a possible source of an authentic sample of 1-ethyl-2-trichloromethylcyclohexane. The reaction mixture was extremely complex, but reluctantly gave up a material which analyzed as $C_9H_{15}Cl_3$. This material coinjected on several vpc columns under several different conditions with the material obtained from the chloroform–octyne reaction. The infrared and nmr spectra of the two samples were generally similar, but not identical. The major differences were in peak intensities and could be the result of the samples being *cis–trans* mixtures of different composition. Both samples were dehydrohalogenated with base to give products with identical vpc retention times. The material obtained by treatment of the chloroform–1-ethylcyclohexene adduct with base gave an infrared absorption at 1617 cm^{-1} and no olefinic absorption in the nmr, as expected[13] for the dehydrohalogenation of a trichloromethylcyclohexane. The approximate relative composition of the chloroform–octyne reaction mixture was: normal monoadducts and allylic isomer (45), cyclopentane derivative (15), and cyclohexane derivative (1).

Discussion

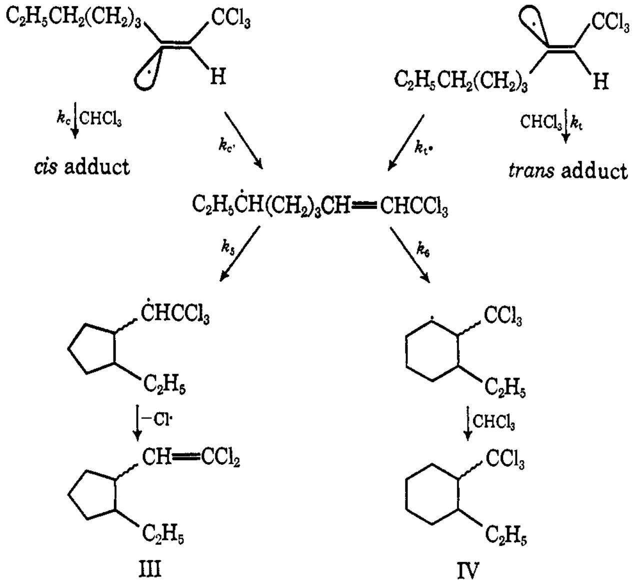
As described in the previous section, the free-radical addition of chloroform to 1-hexyne and 1-octyne is a stereoselective reaction. The kinetically controlled mixture of geometric isomers contains 82 $\pm$ 3% *cis* adduct. The normal, noncyclic adducts can be discussed in terms of the mechanism shown in Scheme I. Previous work demonstrated that neither cumene[1,2] nor thioacetic acid[3] can capture alkyl vinyl radicals before interconversion. The relative rates of reaction of phenyl radicals with chloroform and cumene are not dramatically different.[16] It seems reasonable, therefore, to describe the chloroform additions in terms of equilibrated isomeric vinyl radical intermediates. As previously discussed,[3] the *cis/trans* composition of the product mixture under these conditions is a reflection of the difference in free energies of the transition states leading to the products; the stereochemistry of the initial addition of the trichloromethyl radical to the actylene is not relevant. Thus, the transition state leading to *cis* olefin is preferred by a small amount over that leading to the *trans* isomer. Both adducts rearrange under the reaction conditions to the allylic chloride. Since this rearrangement does not affect the *cis/trans* composition of the mixture, the rate constants for rearrangement of the *cis* and *trans* olefins must be identical.

Scheme I



Cyclic products were observed in the reaction of chloroform with 1-octyne. These are understandable in terms of the abstraction–cyclization scheme reported by Heiba and Dessau[4] (Scheme II). These authors reported an intramolecular reactivity of 1:22 for primary:secondary hydrogens. Thus, the internal abstraction is unimportant in the hexyne reactions, but a significant route to products in the octyne case. The radical formed by this intramolecular abstraction route is partitioned by closure to give five- and six-membered rings.[17] The ratio of rate constants k_5/k_6 is apparently about 15 from the observed yelds of cyclopentane and cyclohexane products.

Scheme II



As indicated, intramolecular abstraction is important in the octyne reaction, but not in the hexyne system. The *cis/trans* composition of the noncyclic adduct mixture, however, is the same for both acetylenes. This is in accord with intermediate mixtures of vinyl radicals which interconvert rapidly with respect to all other fates. If the radicals were not in rapid equilibrium, then the same *cis/trans* product ratio from hexyne and octyne would require that the ratio of rate constants for intramolecular and intermolecular hydrogen abstraction be the same for both the *cis* and the *trans* radicals derived from octyne (*i.e.*, $k_c'/k_c = k_t'/k_t$). A simple steric analysis of the four relevant transition states shows this situation to be improbable; we conclude, therefore, that the intermediate vinyl radicals equilibrate rapidly with respect to other reactions.

Stereoselectivity

The mixture of olefins derived by hydrogen transfer to equilibrated, isomeric 1,2-disubstituted vinyl radicals is often richest in *cis* product. Several authors[2,4,18,19] have suggested that this stereoselectivity is a result of

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(16) R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963).

(17) M. Julia, *Record Chem. Progr.*, **25**, 3 (1964).

(18) A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. M. Bregman, *J. Amer. Chem. Soc.*, **86**, 2877 (1964).

(19) G. D. Sargent and M. W. Browne, *ibid.*, **89**, 2789 (1967).

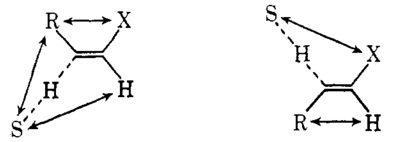
Table I. Steric Interactions for Transition States in Scheme III

Entry	R	X	SH	$T S\Delta G$[a]	G(R–X)[b]	G(S–X)
1	CH_3[c]	C_6H_5	Cumene	0.33	0.78[c]	1.1[h]
2	CH_3[c]	C_6H_5	Cyclohexene	−0.13	0.78[c]	0.65[h]
3	CH_3[c]	C_6H_5	Toluene	−0.21	0.78[c]	0.57[h]
4	C_6H_5[c]	C_6H_5	Cumene	1.5	3.0[d]	4.5
5	C_6H_5[c]	C_6H_5	Cyclohexene	1.0	3.0[d]	4.0
6	*n*-Bu[e]	CCl_3	Chloroform	1.0	~4[f]	~5
7	*n*-Bu[g]	CH_3COS	Thioacetic acid	0.82	0	0.82

[a] Difference in free energy of the isomeric transition states (*trans–cis*) as calculated from the kinetically controlled product composition; in kcalories/mole. [b] Estimated from the difference in free energy of the olefinic products (*cis–trans*) as calculated from the thermodynamically controlled product mixture; in kcalories/mole. [c] Reference 2. [d] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938). [e] This work. [f] The difference in heats of hydrogenation of *cis-* and *trans*-2,2-dimethylpentenes-3 used as a model: R. B. Turner, D. E. Nettleton, and M. Perelman, *J. Amer. Chem. Soc.*, **64**, 1395 (1942). [g] Reference 3. [h] A referee has pointed out that the differences in these values of G(S–X) are in good agreement with the differences in enthalpy of activation for hydrogen transfer observed by Singer and Kong.[2] Apparently, the entropy terms do not vary significantly from solvent to solvent.

steric interactions between the hydrogen donor and the vinyl radical. Approach of solvent to the *cis* radical is less hindered than approach to the *trans* radical; therefore, *cis* product is formed preferentially (*cf.* Scheme III). Singer and Kong established[2] a clear basis for this point of view by demonstrating that, for a given radical, the *cis*/*trans* product ratio increases as the bulk of the hydrogen donor increases. Nevertheless, this steric approach argument is obviously "one-sided." The real problem is to assess the energy difference between the isomeric transition states. Interference between hydrogen donor and the radical is only one of the possible steric sources of this energy difference. It is our intention, in this section, to examine a steric model for the stereoselective behavior of vinyl radicals. Possible electronic origins of the energy differences are ignored.

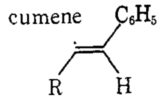
Scheme III



A simple analysis of the transition states for hydrogen abstraction by isomeric 1,2-disubstituted vinyl radicals shows that two types of steric interactions should be important (Scheme III). In the *cis* radical, an R–X steric interaction should increase the transition state energy; in the *trans*, an S–X repulsion raises the energy. Both transition states have S–R interactions which to a first approximation should be equal and, consequently, not contribute to the energy difference between the two species. S–H and R–H repulsions should be small and are assumed to be neglible with respect to the larger R–X and S–X interactions. The energy difference between the two transition states should thus be approximated by [G(S–X) − G(R–X)], a value which can be calculated from the kinetically controlled *trans*/*cis* product ratio. G(R–X) values may be approximated from the thermodynamic *cis*/*trans* olefin ratio. Thus, G(S–X) values can be deduced and examined for consistency and sensibility. The results of this analysis are shown in Table I.

The first three entries in the table are the data of Singer and Kong on the effect of solvent bulk on the *trans*/*cis* product distribution derived from an equilibrated mixture of 1-methyl-2-phenylvinyl radicals. The R–X interaction is constant for these three cases, while the S–X interaction varies with the size of the hydrogen donor. With cumene as the donor, the S–X interaction is greater than the R–X interference, leading to preferential formation of *cis* olefin. With the smaller donors, cyclohexene and toluene, the R–X interaction outweighs the S–X repulsion and the *trans* olefin is favored.

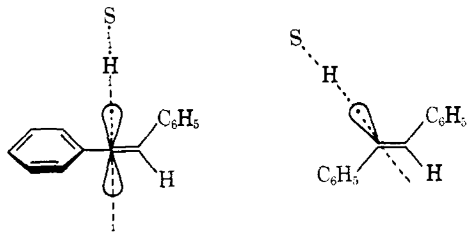
The fourth entry deals with the reaction of the 1,2-diphenylvinyl radical with cumene. The S–X interaction in entries one and four is superficially identical. In both cases, S–X should describe a *cis* interaction between cumene and a 2-phenyl substituent (V). The deduced value of S–X, however, is about four times greater for the 1,2-diphenylvinyl case than for the 1-methyl-2-phenyl case. This clearly indicates a defect in the model. Entries two and five, involving a *cis* interaction between a 2-phenyl substituent and cyclohexene, show a similar lack of agreement.



V

A satisfying resolution of the disagreement between cases one and four (and two and five) involves an sp hybridization for the 1,2-diphenylvinyl radical. Steric interaction of the hydrogen donor with a *cis*-2 substituent should be more important in a linearly hybridized radical than in the bent case, because of the different directions of approach of the donor molecule (Scheme IV). An sp-hybridized, resonance stabilized 1-phenylvinyl radical has been previously invoked[20–22] to explain the enhanced rate of reaction of free radicals with phenyl acetylene. Thus, phenylacetylene captures methyl radicals 16 times more rapidly than does

Scheme IV



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[20] K. W. Doak, *J. Amer. Chem. Soc.*, **72**, 4681 (1950).

[21] M. Gazith and M. Szwarc, *ibid.*, **79**, 3339 (1957).

[22] G. E. Owen, Jr., J. M. Pearson, and M. Szwarc, *Trans. Faraday Soc.*, **61**, 1722 (1965).

methylacetylene.[21] The driving force for the hybridization change in the 1-phenylvinyl radical is proposed[20] to be the stabilization resulting from conjugation of the radical orbital with the aromatic ring.

Molecular orbital calculations[23,24] on the unsubstituted vinyl radical indicate that the esr spectrum is best explained by a radical with an H–C–C angle of 140–150°. We have calculated energy/geometry profiles for the vinyl and 1-methylvinyl radicals using the extended Hückel method.[25] The results (see Experimental Section) reveal an energy minimum when the H–C–C (or C–C–C) angle is 140–150°. Geometric change in the direction of a linear configuration is accompanied by a gradual increase in energy. Distortion toward angles less than 140° leads to sharper increases in the energy of the system. Calculations for the 1-vinylvinyl radical (a model for the 1-phenylvinyl system) indicate that the linear configuration with the radical orbital conjugated with the vinyl substituent is more stable than a bent structure with the π systems conjugated. In summary, an sp-hybridized 1-phenylvinyl radical is suggested by relative reactivity data and calculations, and predicts the anomalously high stereoselectivities observed in hydrogen transfers to the 1,2-diphenylvinyl radical.

The addition of chloroform to 1-hexyne gives a *cis*/*trans* adduct ratio of 82:18. As shown in Table I, this preference for *cis* olefin requires that the chloroform–trichloromethyl interaction (S–X) overcome the *n*-butyl–trichloromethyl repulsion (R–X). This seems to be a reasonable situation since trichloromethyl is approximately isosteric with *t*-butyl.[26]

The addition of thioacetic acid to 1-hexyne gives a kinetically controlled isomer mixture containing 80% *cis* olefin.[3] This result is not readily understandable in terms of a simple steric approach argument. The equilibrium mixture of isomeric olefins is approximately 50:50, indicating essentially no R–X interaction in the products. This value of *G*(R–X), coupled with the energy difference between the two transition states, implies an S–X interaction of ~0.8 kcal/mol. This interaction seems unreasonable on steric grounds. The free energy differences between axial and equatorial cyclohexane positions for $-SC_6H_5$ (model for $SCOCH_3$) and *n*-butyl are 0.6 and 2.1 kcal/mol,[27,28] respectively, indicating that the space-filling properties of *n*-butyl are considerably greater than those of the thiyl substituent. Therefore, in the transition state for the radical reaction, thioacetic acid must certainly have less effective bulk than an *n*-butyl group. Since there is no apparent interference between *n*-butyl and thioacetyl substituents in the products (R–X,) it would be inconsistent to assign a significant steric interaction (S–X) between thioacetic acid and the thioacetyl group in the transition state. Since the steric approach argument fails, the origin of the transition-state energy difference must be sought elsewhere.

The discriminating factor in the reaction of the isomeric 1-butyl-2-thioacetylvinyl radicals with thioacetic acid must serve either to stabilize the transition state leading to *cis* olefin or to destabilize the alternative. It may be that a specific association of the thioacetyl oxygen and the radical, recently suggested[29] by LeBel and DeBoer for additions to cyclohexenes, is operative. This association would be possible only in the *trans* radical and would hinder approach of the hydrogen donor, thereby favoring *cis* olefin.

A preferential stabilization of the *cis*-radical transition state may also be considered. In the esr spectrum[30] of the vinyl radical, the *trans*-β-proton shows an hfs of 68 G, while the *cis*-β-proton has an hfs of 32 G. The 1-methylvinyl radical shows a similar difference in the *trans*-β and *cis*-β hyperfine splittings. Thus, the unpaired spin density at the *trans*-β-proton is about twice that at the *cis*-β-proton. In a system with two different β substituents, it is conceivable that the more stable isomer would be the one with a *trans* arrangement of the radical and the substituent best able to accommodate unpaired spin density. Since the sulfur atom of the thioacetyl substituent should "hold" unpaired spin density better than hydrogen, the *cis* radical should be more stable than the *trans* radical. If this ground-state energy difference is reflected in the corresponding transition-state energies, *cis* olefin would be the preferred product.

In summary, the steric analysis described above gives, in several cases, an acceptable description of the *cis*–*trans* olefin mixtures derived from equilibrated, 1,2-disubstituted vinyl radicals. Apparent exceptions have been observed in the cases of 1-phenyl and 2-thioacetylvinyl radicals. The steric model further allows a number of clear predictions as to the effect of variations in the R–X and S–X interactions.

Experimental Section

All melting points are corrected; boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 421 infrared spectrophotometer. Samples were run as films between sodium chloride plates, except for liquids collected by vpc and authentic materials used for comparison. These were run in chloroform solution in a sodium chloride cavity cell. The nmr spectra were recorded on a Varian A-60 spectrometer in 50% carbon tetrachloride solution with tetramethylsilane as an internal standard. The vpc analyses were performed on a Varian Aerograph A-90-P2 instrument equipped with a thermal conductivity detector and using helium as the carrier gas. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Addition of Chloroform to 1-Hexyne. A flask was fitted with a total condensation variable take-off still head. This system was connected through the still head to an open-end mercury manometer, which was joined to a water aspirator and a tank of dry nitrogen by a three-way stopcock. Purified reactants and glass boiling beads were placed in the flask and cooled to 0°. The system was evacuated to 6.5 cm and filled to atmospheric pressure with dry nitrogen five times. The system was maintained at reflux (62°) under a positive pressure of nitrogen. When the desired reaction time was reached, the condenser was changed from total reflux to total take off. Material was distilled until the head temperature reached 72°; the remaining volatile materials were then removed at room temperature with a rotary evaporator. The residue was a viscous yellow-orange liquid. This liquid was taken up in 100 times its volume of petroleum ether (bp 30–60°). White crystals of benzoyl peroxide formed as the solution cooled. The crystals were filtered off, and the petroleum ether was removed on the rotary evaporator. This process was repeated until no more crystals were

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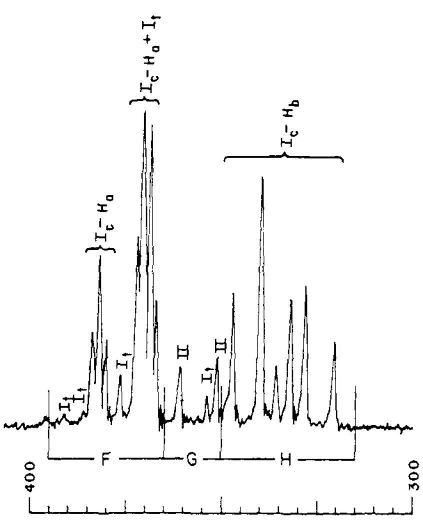

Figure 1. 60-MHz spectrum of a typical chloroform–1-hexyne reaction mixture showing the peak assignments and the basis of the analysis; the scale is in hertz with respect to TMS.

obtained. The resulting viscous orange liquid was washed with three 500-ml portions of 5% sodium bicarbonate solution, dried for 5 hr over magnesium sulfate, and distilled at 1.5 mm. Fractions were collected until the pot temperature reached 120°; by then only black tar remained in the distilling flask. Data for a typical 5-hr run follow. Reagents: 1-hexyne (15 g, 0.17 mol), distilled twice under nitrogen, bp 70–71°, n^{24}D 1.3980; 31 g (0.13 mol) of benzoyl peroxide, recrystallized twice from chloroform, mp 104–105°; 200 ml (1.67 mol) of chloroform, bp 61–62°, ethanol removed with sulfuric acid. Products: monoadducts (4.65 g, 0.023 mol), bp 50–55° (1.5 mm), 13.5% yield based on starting hexyne; 5.3 g of black tar.

The vacuum distillation of the crude reaction mixture gave a material which distilled over smoothly between 50 and 55° (1.5 mm). Only a few drops of material were collected before and after the main fraction. The product was redistilled under vacuum through a 1-ft Vigreux column; fractions were cut when 0.5 ml of material had been collected. Samples distilled were 5.0 ml or larger in size. Infrared and nmr spectra showed a change in the relative strength of certain peaks for the series of fractions. In going from the first fraction to the last, the infrared band at 1620 cm^{-1} increased while bands at 1640 and 1650 cm^{-1} decreased; the nmr doublet at τ 4.05 and the sextet at 5.40 grew while all other peaks in the 3.5–5.0 region lost strength.

The relative intensities of the spectral peaks also changed with the reaction time. The first two cuts ($I_{c,t}$) of a reaction mixture run for less than 5 hr showed no 1620-cm^{-1} band and no τ 4.05 doublet. The last two cuts (II) of a reaction mixture run for more than 200 hr showed no trace of the 1640- and 1650-cm^{-1} bands and had only the τ 4.05 doublet and 5.40 sextet in the vinyl region. $I_{c,t}$: n^{25}D 1.4751; infrared 3020 (w), 1650 (w), 1640 (s), 820 (s), 790 (s), and 710 cm^{-1} (w); nmr τ 4.07 (multiplet, 2 H), 7.5 (multiplet, 2 H), 8.6 (multiplet, 4 H), 9.1 (triplet, $J = 7$ Hz, 3 H). II: n^{25}D 1.4749; infrared 3020 (w), 1620 (s), 830 (m), 720 (w), and 700 cm^{-1} (w); nmr τ 4.05 (doublet, $J = 9.8$ Hz, 1 H), 5.40 (doublet of triplets, J = 9.8 and 6.6 Hz, 1 H), 8.6 (multiplet, 4 H), and 9.1 (triplet, $J = 7$ Hz, 3 H).

Anal. Calcd for $C_7H_{11}Cl_3$: C, 41.78; H, 5.50; Cl, 52.78. Found for $I_{c,t}$: C, 42.02; H, 5.58; Cl, 52.68. Found for II: C, 42.01; H, 5.59; Cl, 52.72.

Vapor phase chromatography of $I_{c,t}$, I_t, and II was attempted on several columns under several conditions of flow rate and temperature. Stainless steel, aluminum, and glass columns were tried in connection with Craig polyester, Dow 11, SF-96, and QF-1 liquid phases on 30–60 Chromosorb P. No conditions were found where different patterns could be obtained from $I_{c,t}$, I_t, and II. Metal columns gave nonreproducible chromatograms showing anywhere from 1 to 16 peaks. The glass column, used in connection with a glass injector port liner gave a single reproducible peak from all three samples. This peak was collected from each sample; the nmr spectra of the collected materials were all identical with the nmr of II.

Preparation of *trans*-1,1,1-Trichloroheptene-2 (I_t). 1-Hexene was distilled twice under nitrogen, bp 62–63°, n^{25}D 1.3822. Bromotrichloromethane was distilled three times under nitrogen, bp 104–105°, n^{25}D 1.5297. 1-Hexene (14.7 g, 0.18 mol) and bromotrichloromethane (49 g, 0.25 mol) were combined in a Pyrex flask and irradiated at room temperature for 1 hr with a 0.15-A, long-wavelength uv lamp (Model x-4, Ultraviolets Products, Inc., South Pasadena, Calif.). The unreacted materials were removed to give 51.7 g of a yellow liquid. This was distilled at 82–84° (2 mm) to give 33.5 g (0.12 mol) of 3-bromo-1,1,1-trichloroheptane, n^{25}D 1.4950, 66% yield. The infrared spectrum of the reaction product showed no absorption from 1600 to 1700 cm^{-1} and strong bands at 710 and 795 cm^{-1}.[7,31]

The nmr spectrum showed a multiplet at τ 5.72 (one proton), an octet at 6.69 (two protons), a multiplet at 8.10 (two protons), a multiplet at 8.68 (four protons), and a triplet at 9.1 (three protons).[7]

3-Bromo-1,1,1-trichloroheptane (54.3 g, 1.9 mol) was dissolved in 50 ml of 95% ethanol and cooled to 0°, and a solution of 13 g of potassium hydroxide in 70 ml of 95% ethanol was added dropwise with stirring. The solution was stirred for 15 min after the addition was completed, and then was added to 500 ml of water. The aqueous and organic layers were separated, and the water layer was washed with three 100-ml portions of chloroform. The chloroform washings and the organic layer were combined and dried over magnesium sulfate. The chloroform was removed and the resulting 36.9 g of yellow liquid was distilled under vacuum to give 27.3 g (1.36 mol, 70% yield) of *trans*-1,1,1-trichloroheptene-2 (I_t), n^{25}D 1.4602, bp 50–55° (1.5 mm); infrared: 3020 (w), 1650 (m), 830 (m), 775 (s), and 705 cm^{-1} (m); nmr: τ 3.82 (multiplet, 2 H), 7.48 (multiplet 2 H), 8.6 (multiplet 4 H), 9.1 (triplet, $J = 7$ Hz, 3 H).

Anal. Calcd for $C_7H_{11}Cl_3$: C, 41.78; H, 5.50; Cl, 52.78. Found: C, 41.84; H, 5.55; Cl, 52.53.

The second-order nmr spectrum due to the olefinic protons of I_t was resolved with the aid of a computer analysis using LAOCOON-II.[9] The parameters used in the calculations were: number of spin $^1/_2$ nuclei, 4; lower limit of frequency range, 300.0; upper limit of frequency range, 450.0; minimum allowable intensity, 0.050; isovalues, 1 for all nuclei; and line-spacing parameter, 0.300. Agreement between the observed spectrum and the calculated spectrum was achieved to within 1.0 Hz with the following values: H_a, 366; H_b, 374; $2H_c$, 129; $J_{ab} = 16.4$, $J_{ac} = -2.0$, $J_{bc} = 7.5$, $J_{cc} = -13.0$ Hz.

Quantitative Analysis of Trichloroheptene Mixtures by Nmr. All nmr peaks from chloroform–1-hexyne reaction mixtures could be explained on the basis of I_c, I_t, and II. The integrated nmr spectra from these reaction mixtures were used to obtain the relative amounts of the trichloroheptenes. Integrals of the spectra were run at 100 Hz full scale offset 300 Hz from tetramethylsilane. Before a series of quantitative runs were made, the instrument was carefully adjusted using a water sample. Six integrals were made of each sample, three with upfield sweep and three with downfield sweep; the percentages given are the average of the six determinations for each sample. The integrated spectra were divided into three sections. The integral area from 395 to 365 Hz (F) from tetramethylsilane was assigned to the two vinyl protons of I_t and to one proton from I_c. The area from 365 to 350 Hz (G) was assigned to the olefinic proton of II, and the area from 350 to 315 Hz (H) was assigned to the second vinyl proton of I_c (Figure 1). These assignments are in accord with the spectra of pure I_t and II, and with the first-order pattern observed for I_c. There appeared to be no interfering signals in the distilled samples. The per cent of II relative to total trichloroheptenes and the per cent of I_c relative to $I_{c,t}$ were calculated from the following formulas: $\%\ II = 2G/F + H + 2G$; $\%\ I_c = 2H/(F + H)$. The sample described in Table II was reanalyzed every 1 or 2 days to check the reproducibility of the method. The sample was stored at 0° between runs. Six analyses on different days gave the following values for % I_c: 78.5 ± 2, 80.4 ± 2, 85.0 ± 3, 78.7 ± 3, 80.9 ± 2, 81.0 ± 2; average = 80.8 ± 2.

Allylic Rearrangement of 1,1,1-Trichloroheptene. 1. Thermal. A mixture (1.03 g) composed of 14% II and 86% $I_{c,t}$ was added to 250 ml of chloroform (ethanol not removed) and the resulting solution was refluxed for 48 hr; the chloroform was removed to give 0.98 g of a colorless liquid. An nmr analysis showed the material contained 35% II and 65% $I_{c,t}$. The percentage of I_c relative to $I_{c,t}$ remained constant at 81 ± 2%.

2. Radical Catalyzed. Benzoyl peroxide (4.98 g), $I_{c,t}$ (8.13 g), and 100 ml of ethanol-free chloroform were combined and heated

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Table II. Typical Chloroform-1-Hexyne Addition Analysis

Integral no.	Direction of sweep	Area[a] *F*	*G*	*H*	% I_c[b]	% II[c]
1	Upfield	107	11	65	75.6	11.3
2	Upfield	105	12	67	77.9	12.2
3	Upfield	106	12	67	77.5	12.2
4	Downfield	104	12	68	79.1	12.2
5	Downfield	105	13	68	78.8	13.0
6	Downfield	98	12	68	81.9	12.6

Average Values
$\% I_c = 78.5 \pm 2$[d]
$\% II = 12.2 \pm 1$[d]

[a] In arbitrary units. [b] $\% I_c = 10^2 I_c/I_{c,t}$. [c] $\% II = 10^2 II/(I_{c,t} + II)$. [d] Precision given as standard deviation.

to reflux under the conditions used for the addition of chloroform to 1-hexyne. Several 10-ml samples were removed during the reaction and worked up in the manner used for samples from the addition reaction. The composition of the samples was determined by nmr analysis of the distilled products. The infrared and nmr spectra of the distilled material showed only signals which could be assigned to $I_{c,t}$ or II (Table III). The last sample showed several small unidentified peaks in the vinyl region of the nmr before distillation. The amount of I_c relative to $I_{c,t}$ remained constant at 81 ± 2% for the first three samples.

Table III. Radical-Catalyzed Rearrangement of $I_{c,t}$

Period of reflux, hr	% II	Period of reflux, hr	% II
0	0	24	86
10	25	48	100

3. Lewis Acid Catalyzed. $I_{c,t}$ (0.48 g) was dissolved in chloroform and allowed to stand in contact with aluminum chloride for 12 hr at room temperature. The liquid was decanted and the chloroform removed to give 0.47 g of material with infrared and nmr spectra identical with those of II.

Isomer Stability of $I_{c,t}$. 1. The products from the addition of chloroform to 1-hexyne were studied as a function of time. Several additions were run where 10-ml samples were withdrawn periodically from the reaction vessel, worked up, and analyzed by nmr. Data from a typical reaction are shown in Table IV.

Table IV. Effect of Time on the Isomeric Composition of Products from the Reaction of Chloroform with 1-Hexyne[a]

Time, hr	Yield[b] of $I_{c,t}$ + II, %	Yield[b] of $I_{c,t}$, %	$10^2 I_c/I_{c,t}$
10	17	17	82
30	47	47	81
70	85	70	83
130	57	7	80
250	21	0	

[a] Initial concentrations: 1-hexyne, 0.44 *M;* benzoyl peroxide, 3.0 *M.* [b] Based on 1-hexyne.

2. Mixtures of $I_{c,t}$ and I_t were prepared and analyzed by nmr. These mixtures were added to chloroform solutions containing benzoyl peroxide (*ca.* 2 *M*), and the resulting solutions were refluxed under nitrogen; samples were withdrawn periodically and analyzed by nmr (Table V).

3. *trans*-1,1,1-Trichloro-2-heptene, I_t (2.4 g), was mixed with 5 ml of 1-octyne, 30 ml of chloroform, and 1.24 g of benzoyl peroxide. This mixture was refluxed under nitrogen for 6 hr and worked up in the standard manner to give 3.8 g of material, bp 50–80° (1.5 mm). This was redistilled through a 1-ft Vigreux column. Three fractions were collected, 0.23 g at 50–52°, 2.81 g at 52.75°, and 0.36 g at 70–75°. The first and second fractions were found by nmr to be a mixture of I_t and II in 80:20 ratio; the I present was 100% *trans*. The last cut was a mixture of 1,1,1-trichlorononene-2 and 1,1,3-trichlorononene-1 in a 90:10 ratio. The 1,1,1-trichlorononene-2 was 80% *cis*, 20% *trans.*

Table V

Mixture	Time, hr	$10^2 I_c/I_{c,t}$	% II
1	0	83.2	0
	8	80.1	30
	16	81.6	90
2	0	56.8	0
	6	58.3	25
	14	54.7	80
3	0	25.4	0
	8	25.0	75
	12	23.8	90
4	0	0	0
	4	0	50
	9	0	90

Ozonization. The apparatus consisted of a tank of dry oxygen connected through a flow meter to a 1.5-m Berthelot tube, powered by a 9000-V transformer. From the Berthelot tube, the gas passed through the ozonization cell and then through two bubblers containing 5% potassium iodide solution.

1. I_t (1.18 g, 0.586 mmol) was dissolved in 10 ml of ethyl acetate and cooled to −80°. A stream of ozone in oxygen was passed through the solution for 45 min, until a sky blue color was apparent. Oxygen was then passed through the solution until the color disappeared. The solution was warmed to room temperature and the ethyl acetate removed to give 1.30 g of ozonide as a colorless liquid: infrared 2960 (s), 2940 (s), 2280 (m), 1750 (m), 1628 (w), 1470 (m), 1407 (w), 1383 (m), 1360 (m), 1300 (w), 1245 (m), 1120 (s), 1100 (m), 1050 (m), 990 (m), 950 (w), 870 (w), 845 (m), 825 (m), 804 (s), 750 (m), 700 (w), and 620 cm^{-1} (m); nmr τ 4.5 (multiplet, 2 H), 8.3 (multiplet, 2 H), 8.6 (multiplet, 4 H), and 9.18 (triplet, 3 H).

$I_{c,t}$ (0.650 g) in 10 ml of ethyl acetate was treated in the same manner and yielded 0.813 g of a colorless liquid. This material gave infrared and nmr spectra which differed from the product from I_t only in the relative intensities of several peaks. The difference was most apparent in the τ 4.5 multiplet in the nmr spectrum. The τ 4.5 multiplet could be analyzed as a triplet at 4.72 and a singlet at 4.41 with equal intensities and a triplet at 4.42 and a singlet at 4.48 with equal intensities by comparison of the nmr spectra of the ozonide mixtures from $I_{c,t}$ and I_t. The product from I_t showed an intensity ratio of 20:80 for the τ 4.72–4.41 pattern relative to the 4.42–4.48 pattern; the product from $I_{c,t}$ showed a 40:60 ratio.

2. I_t (1.47 g, 7.26 mmol) and TCNE[11] (1.08 g, 8.46 mmol) were dissolved in 17.7 g of ethyl acetate and cooled to −80°. A mixture of ozone in oxygen was passed through the solution for 60 min until a blue color was observed. A stream of dry nitrogen was then bubbled through the solution until the color disappeared. This solution was warmed to room temperature and analyzed by vpc. The mole ratio of the aldehydes was calculated from the observed peak height ratios by the use of a proportionality constant determined with standard solutions. Absolute yields of the aldehydes were determined by doping known weights of the reaction mixture with known weights of the two aldehydes and observing the change in the mole ratio. This analysis indicated an 85% yield of valeraldehyde and an 81% yield of chloral. Peaks thought to be chloral and valeraldehyde were collected from undoped samples of the reaction mixture and gave infrared spectra identical with those of authentic chloral and valeraldehyde.

3. In a similar ozonolysis of I_t, the nitrogen purge of excess ozone was omitted. Vpc analysis indicated only a 30% yield of valeraldehyde and a 46% yield of chloral. The reaction mixture was then distilled to give two fractions, bp < 78° and bp 78–110°. Treatment of the latter fraction with 2,4-dinitrophenylhydrazine reagent gave a mixture of products. Two recrystallizations of this crude material from ethanol gave a 15% yield of the 2,4-dinitrophenylhydrazone of chloral, mp and mmp 273–275°. The mother liquid from the first ethanol recrystallization was concentrated and the resulting solid was recrystallized twice from ethyl acetate to give 9.9% of the 2,4-dinitrophenylhydrazone of valeraldehyde, mp and mmp 104–105°.

4. An ozonolysis of $I_{c,t}$, as described in section 2 above, gave a 62% yield of chloral and a 53% yield of valeraldehyde. Peaks thought to be due to chloral and valeraldehyde were collected and gave infrared spectra identical with those of the authentic materials.

5. When II was treated with ozone, the blue color appeared within 15 min. Subsequent work-up and vpc analysis gave no detectable response for valeraldehyde and chloral under conditions where a 0.25% yield of either aldehyde was readily observable. Removal of the solvent gave a 92% yield of recovered II and infrared and nmr spectra identical with those of authentic material.

Photoreaction of Benzophenone, Benzoyl Peroxide, 1-Hexyne, and Chloroform. A solution of 1-hexyne (1.32 *M*), benzoyl peroxide (0.35 *M*), and benzophenone (0.043 *M*) in chloroform was prepared. Samples (10 ml) of the solution were degassed, sealed in Pyrex tubes, and irradiated with a high-pressure mercury lamp under four different conditions of time and temperature. After irradiation, the tubes were opened and their contents worked up in the manner used for the thermal addition reactions. The results are given in Table VI. The nmr spectrum was analyzed in detail to obtain the isomeric composition of the product. In each case, the product distilled at 50–55° (0.9 mm) and gave nmr and infrared spectra identical with those of 1,1,1-trichloroheptene-2.

Table VI. Effect of Temperature on the Addition of Chloroform to 1-Hexyne

Temp, °C	Irradiation time, hr	% yield[a]	$10^2I_c/I_{c,t}$
17	4.8	6	80
17	10.0	10	78
0	5.1	4	82
0	10.3	13	79

[a] Based on 1-hexyne.

A solution of benzoyl peroxide (0.5 g, 2 mmol), benzophenone (0.1 g, 0.6 mmol), and *trans*-1,1,1-trichloroheptene-2 (1.0 g, 5 mmol) in 10 ml of chloroform was prepared. This solution was placed in a Pyrex tube which was degassed, sealed, and irradiated for 10 hr. Normal work-up gave 0.46 g of material which was shown by nmr analysis to be 95% *trans*-1,1,1-trichloroheptene-2 and 5% 1,1,3-trichloroheptene-1. *cis*-1,1,1-Trichloroheptene-2 was not observed.

The Addition of Chloroform to 1-Octyne. A solution of 18.0 g (0.16 mol) of 1-octyne and 25.0 g (0.10 mol) of benzoyl peroxide in 200 ml of ethanol-free chloroform was refluxed under nitrogen for 5.5 hr. The procedures used for the reaction and the work-up were identical with those used in the addition of chloroform to 1-hexyne. From this reaction, 8.51 g of a clear, colorless liquid, bp 56–78° (0.3 mm), and 5.65 g of a red tar were obtained. The colorless reaction product was redistilled (0.3 mm) through a 3-ft Vigreux column to yield four fractions: *S*, 0.8 g at 55–57°; *T*, 2.5 g at 59–62°; *U*, 4.4 g at 67–75°; and *V*, 0.6 g at 75–80°.

The infrared spectrum of *S* showed a strong band at 1630 cm^{-1} with a small shoulder at 1620 cm^{-1}: *S* nmr τ 3.8–4.4 (multiplet, 1.8 H), 7.6 (multiplet, 2.1 H), 8.7 (multiplet, 8.1 H), and 9.1 (triplet, J = 7 Hz, 3 H). *S* gave no precipitate with ethanolic silver nitrate after 12 hr at room temperature and is tentatively assigned as 1-chlorooctene-1.

Anal. Calcd for $C_8H_{15}Cl$: C, 65.11; H, 10.18; Cl, 24.71. Found for *S:* C, 65.52; H, 10.31; Cl, 24.17.

Vpc analysis of *T* on 20 ft × 0.25 in. Dow 11 on Chromosorb P column, column temperature 80°, and flow rate 60 cc/min, gave two major peaks of about equal area at 25 and 28 min. These were collected from repeated injections to give two materials, *J* and *K;* both samples were found, upon reinjection, to be homogeneous (>98%). Infrared spectra of both compounds showed a band at 1618 cm^{-1}: *J* nmr τ 4.35 (doublet, J = 10.0 Hz, 1 H), 7.3–8.9 (multiplet, 10 H), and 9.1 (triplet, J = 7 Hz, 3 H); *K* nmr τ 4.41 (doublet, J = 9.2 Hz, 1 H), 7.3–8.9 (multiplet, 10 H), and 9.1 (triplet, J = 7 Hz, 3 H). Neither *J* nor *K* gave a precipitate with ethanolic silver nitrate after 24 hr at room temperature. These compounds are assigned as *cis*- and *trans*-1-ethyl-2-(β,β-dichlorovinyl)-cyclopentane.[4]

Anal. Calcd for $C_9H_{14}Cl_2$: C, 55.97; H, 7.31; Cl, 36.72. Found for *J:* C, 56.19; H, 7.47; Cl, 36.51. Found for *K:* C, 55.81; H, 7.50; Cl, 37.00.

U gave an infrared spectrum identical with the spectrum of the trichloroheptene mixture obtained from the addition of chloroform to 1-hexyne. The nmr spectra of the materials differed only in the intensity of the methylene multiplet; the material, *U*, had a multiplet at τ 8.8 equivalent to eight protons (the methyl triplet being set equal to three protons) while the multiplet at 8.8 in the trichloroheptene adduct was equivalent to four protons. *U* could be isomerized with ethanolic potassium hydroxide to give a material whose infrared and nmr spectra were identical with those obtained for 1,1,3-trichlorononene-1, prepared by the bromotrichloromethane addition route. An analysis of the *cis–trans* composition of the octyne–chloroform adduct was carried out by nmr as described for the 1-hexyne adduct case. The products from four separate additions yielded a value of 82 ± 3% *cis*-1,1,1-trichlorononene-2.

Anal. Calcd for $C_9H_{15}Cl_3$: C, 47.08; H, 6.59; Cl, 46.33. Found for *U:* C, 47.02; H, 6.85; Cl, 46.18. Found for isomerized *U:* C, 46.81; H, 6.73; Cl, 46.12.

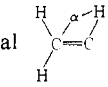
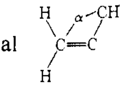
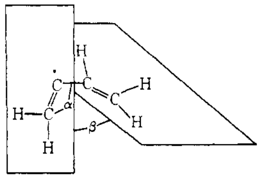
The infrared and nmr spectra of *V* showed all the lines found in *U* plus several additional peaks. *V* was analyzed by vpc on a 20-ft Dow 11 on Chromosorb P column, column temperature 150°, flow rate 100 cc/min. Three major peaks were seen at 11.5, 16.2, and 21.0 min, with relative areas of 5:50:1. Under the same conditions, *trans*-1,1,1-trichlorononene-2 (prepared by the authentic dehydrohalogenation route), 1,1,3-trichlorononene-1 (prepared by potassium hydroxide rearrangement of 1,1,1-trichlorononene-2), and the mixture of trichlorononene isomers from *U* all gave peaks at 11.5 and 16.2 min. The peak at 21.0 min was collected and upon reinjection gave a single peak. This material was assigned as 1-ethyl-2-trichloromethylcyclohexane. The nmr showed peaks at τ 7.6 (multiplet), 7.8–8.9 (multiplet), and 9.1 (triplet, J = 7 Hz). The infrared spectrum had bands at 2990 (s), 2800 (s), 1450 (s), 1375 (m), 1283 (m), 1210 (m), 1190 (m), 990 (w), 910 (m), 870 (w), 765 (s), 750 (s), 720 (w), and 695 (s) cm^{-1}.

Anal. Calcd for $C_9H_{15}Cl_3$: C, 47.08; H, 6.59; Cl, 46.33. Found: C, 47.39; H, 6.41; Cl, 45.98.

The 1-ethyl-2-trichloromethylcyclohexane (20 μl) was dissolved in 1 ml of ethanolic potassium hydrochloride and allowed to stand for 15 min at room temperature. Work-up gave 0.009 g of a clear, colorless liquid. Both the starting material and the dehydrohalogenated product coinjected on three vpc columns under two conditions with materials prepared by the addition of chloroform to 1-ethylcyclohexene.

1-Ethyl-2-trichloromethylcyclohexane. 1-Ethylcyclohexene (24.6 g, 0.223 mol) and 28.9 g (0.119 mol) of benzoyl peroxide were dissolved in 2 l. of ethanol-free chloroform. The mixture was cooled

Table VII[a]

α, deg	β, deg	E_c	E_r	E_t
		Vinyl Radical		
120		−168.7123	−11.4083	−180.1206
135		−169.0945	−11.1899	−180.2844
150		−169.3371	−10.9923	−180.3294
165		−169.4714	−10.8533	−180.3245
180		−169.5143	−10.8030	−180.3174
		1-Methylvinyl Radical		
90		−263.7787	−11.9740	−275.7527
100		−265.1399	−11.7975	−276.9374
110		−266.0210	−11.5618	−277.5828
120		−266.5775	−11.3257	−277.9033
130		−266.9340	−11.1037	−278.0377
140		−267.1789	−10.8874	−278.0662
150		−267.3363	−10.7033	−278.0396
160		−267.4361	−10.5583	−277.9944
170		−267.4909	−10.4655	−277.9564
180		−267.5085	−10.4350	−277.9436
		1-Vinylvinyl Radical		
120	0	−333.4473	−11.4336	−344.8809
180	0	−334.3368	−10.5256	−344.8624
180	90	−334.3729	−10.8323	−345.2053

[a] Energies are measured in electron volts.

to 0°, and deoxygenated by evacuating to 5 cm and filling with nitrogen seven times. The solution was refluxed for 67 hr; at the end of that time it was clear and colorless. The solution was stripped to 200 ml and washed with three 200-ml portions of sodium bicarbonate. The solution was then dried over magnesium sulfate and the remaining chloroform removed to give 67.5 g of a slightly yellow oil. This material (35.7 g) was distilled (2.5 mm) to give five fractions: 1.21 g, bp 30–90°; 6.69 g, bp 90–100°; 7.38 g, bp 100–120°; 8.92 g, bp 120–125°; and 5.75 g of orange residue. Fraction 1 was recovered 1-ethylcyclohexene; fractions 3, 4, and 5 all showed aromatic absorbtion in the infrared and nmr. Fraction 2, bp 90–100°, was examined by vpc (20 ft × 0.25 in. Dow 11 column at 140°, flow rate 70 cc/min) to give peaks at 21.0 and 22.8 min with relative areas of 1:1.8. Both materials were collected from repeated injections. The sample of shortest retention time was found to still be a mixture of the two original materials by reinjection. This material showed olefinic absorption in the infrared and nmr and was not further investigated.

The sample of longest retention time (22.8 min) was homogeneous (>99%) on reinjection: infrared 2990 (s), 2900 (s), 1450 (s), 1380 (m), 1200 (w), 1040 (m), 1030 (w), 950 (m), 930 (m), 910 (m), and 765 (s) cm^{-1}; nmr τ 7.6 (multiplet, 2 H), 7.9–8.9. (multiplet, 10 H), and 9.1 (triplet, J = 7 Hz, 3 H). This material did not give a precipitate with ethanolic silver nitrate in 2 hr at room temperature and was assigned as 1-ethyl-2-trichloromethylcyclohexane (IV).

Anal. Calcd for $C_9H_{15}Cl_3$: C, 47.08; H, 6.59; Cl, 47.33. Found: C, 47.17; H, 6.38; Cl, 46.15.

1-Ethyl-2-trichloromethylcyclohexane (0.135 g) was dissolved in 95% ethanolic potassium hydroxide solution. The mixture immediately became cloudy. After 15 min at room temperature, the solution was worked up by extraction to give 0.071 g of a clear, colorless liquid. The infrared spectrum of this material showed a moderately strong band at 1617 cm^{-1}. The nmr showed a multiplet at τ 7.3 (3.3 H), a multiplet at 7.6–8.8 (7.7 H), and a triplet (J = 7 Hz) at 9.1 (3 H). The dehydrohalogenation product did not react with ethanolic silver nitrate solution after 12 hr at room temperature.

Addition of Bromotrichloromethane to 1-Octene. The photoaddition of bromotrichloromethane to 1-octene gave 1,1,1-trichloro-3-bromononane, bp 98–100° (0.9 mm) (lit.[32] bp 99–102° (0.6 mm)), in 80% yield. Dehydrohalogenation of this material, as described for the hexene adduct, gave 70% of 1,1,1-trichlorononene-2, bp 76–79° (0.9 mm), n^{23}D 1.4750 (lit.[32] bp 70–75° (0.6 mm), n^{26}D 1.4758). A detailed nmr analysis of this material showed it to be solely the *trans* isomer.

Molecular Orbital Calculations. An extended Hückel program[25] supplied by the Quantum Chemistry Program, Indiana University, was modified for use on an IBM 7074 computer. The program as used could handle a maximum of six hydrogens and six first-row elements in one molecule. The following parameters were used in the calculations: K in Wolfsberg–Helmholtz approximation,[24] 1.5; C–H bond length, 1.10 Å; C–C bond length, 1.54 Å; C=C bond length, 1.34 Å; Slater exponent for carbon, 1.625; H_{ii}2s, 21.40 eV; H_{ii}2p, 11.40 eV.

In reporting the results of these calculations, the geometry of the system is given in Table VII together with the sum of all energy levels below the radical orbital, E_c (the energy of the corresponding carbonium ion), E_r (the energy of the radical orbital), and E_t (the total energy of the radical).

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The Stereochemistry of Addition Reactions of Allenes. I. Methoxymercuration and Halogenation of 1,3-Dimethylallene[1,2]

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Abstract: A procedure for the partial resolution of 1,3-dimethylallene by asymmetric hydroboration is described. The $(-)$ enantiomer is assigned the *R* configuration. The stereochemistry of electrophilic addition of mercuric acetate in methanol to optically active 1,3-dimethylallene has been determined by relating the configuration of the dissymmetric allene to the configuration of the major asymmetric adduct. Similarly, the orientation and stereochemistry of halogen addition to $(-)$-1,3-dimethylallene in carbon tetrachloride, ether, and methanol have been studied. The results of this work establish that oxymercuration and halogenation of 1,3-dimethylallene under the conditions studied are stereospecific *trans* additions. These reactions and their stereochemistry are discussed with reference to the types of intermediate cations that may participate.

The mechanisms of addition reactions of allenic compounds are interestingly complex because of the numbers of different types of reaction intermediates that can in principle be involved. For example, addition of an electrophilic reagent (X^+) to an allene could generate a vinyl cation (A), a nonplanar allylic cation (B), or a bridged ion (C), depending on whether initial attack by the electrophile occurs at the terminal carbon, the central carbon, or at both (eq 1).

The possibility exists that these intermediates may interconvert and, in particular, the cation B may undergo rapid bond rotation to give the planar resonance-stabilized allylic ion D. The situation becomes even more diverse if the geminal substitutents at the terminal allenic carbons are different, as in 1,3-disubstituted allenes, since there are now two directions of approach of the reagent X^+ and hence two stereochemically different sets of ions to consider as possible intermediates.

Some information as to the types of intermediates involved can be inferred from studies of the orientation of addition of unsymmetrical reagents to allenes and, in fact, most of the reported studies of electrophilic,

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