

two parallel second-order reactions involving a common reactant, preceded by an equilibrium between the common reactant and each of the other two reactants, leads to the expression

$$k_X/k_H = k_X'K_X/k_H'K_H$$

for the experimentally observed ratio of rate constants for disappearance by addition. An interpretation of the polar effects observed then resolves itself into an assessment of the effect of a substituent in the phenyl group on the ratio of the equilibrium constants for the complexation step, K_X/K_H , and the ratio of the rate constants for the intramolecular addition step, k_X'/k_H' . The effect of substituents on the ratio K_X/K_H can be predicted confidently. Complexation is favored by a high basicity or high electron density on the part of the aromatic π -system.^{40-43, 46, 47} Thus electron-donating groups favor complexation and cause the value of the ratio K_X/K_H to exceed unity, while electron-withdrawing groups retard complexation and lower the value of K_X/K_H to below unity. In other words, the complexation step has a negative ρ -value. A prediction of the effect of a ring substituent on the k_X'/k_H' ratio requires consideration of several kinetic situations. It is likely that the intramolecular addition step takes place quite rapidly, since the complexed radical is being held in the vicinity of the double bond with which it ultimately reacts. Thus, the transition state for ultimate addition should resemble the π -complex to a much greater extent than it resembles the final adduct radical. This being the case, a ring substituent will have virtually no effect on k_X' and the ratio k_X'/k_H' will be insensitive to the nature of ring substituents. Hence, the observed polar effect is a consequence of the influence of the substituent on the equilibrium preceding addition, and a negative ρ -value will be observed as long as the benzene ring and the double bond are in the same molecule and intramolecular addition is possible, and the presence of methylene groups between the ring and the double bond will not diminish the effect. The limiting case of the above kinetic situation would be one in which the addition step were so fast that the reverse of complexation, that is, dissociation, could not compete, thereby making the "equilibrium" irreversible, whereupon the observed polar effect would fall into the rate constant for complexation. Only in the event that the rate constant for addition were decreased (by ground state stabilization of the complex relative to the transition state for addition) by the same amount that the equi-

librium constant for complexation were increased (by stabilization of the complex relative to the dissociated parents), would the effect of a substituent on the observed relative rates of disappearance of two olefins be negligible (since K_X/K_H would be increased and k_X'/k_H' decreased by the same factor). This situation is unlikely, however, since the transition state for the addition step will be close enough on the reaction coordinate to the complex that structural features which stabilize or destabilize one will have the same effect upon the other. From this discussion it can be seen that the postulation of an equilibrium step preceding the addition step provides an explanation for the observed polar effects in the addition reactions of the trichloromethyl radical to the double bond of the two series studied.

The formation and importance of complexes is supported by several other features as well. The very high rate of addition to abstraction is probably a consequence of complexation. The complexed trichloromethyl radical would be a less reactive, and hence more selective species, than an uncomplexed trichloromethyl radical. Thus, the lower activation energy process, addition, would tend to be favored at the expense of the higher activation energy process, abstraction. A geometric factor would also favor addition, since the pendant side chain can adopt conformations in which the terminal double bond passes close to the region over the benzene ring which would be occupied by the complexed trichloromethyl radical, whereas the proper orientation for hydrogen abstraction from the side chain of the complexing aromatic would be less readily achieved.⁴⁸ This is particularly true of the 4-phenyl-1-butenes.

Further implications relating to the steric requirements of intramolecular addition within π -complexes are explored in the next paper,³⁹ which reports studies of the reactions of the trichloromethyl radical with a series of phenylalkenes in which the double bond occupies different positions with respect to the benzene ring.

Acknowledgment.—It is a pleasure to thank the donors of the Petroleum Research Fund for a grant (PRF No. 603-A) administered by the American Chemical Society, which financed the greater part of this work.

(48) Intramolecular abstraction reactions by chlorine atoms complexed with *n*-butylbenzene could not be detected: G. A. Russell, A. Ito, and D. G. Hendry, *J. Am. Chem. Soc.*, **85**, 2976 (1963). This work was brought to our attention by a referee.

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The Addition of the Trichloromethyl Radical to ω -Phenylalkenes

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It has been found that the reactivity of the double bond in the series $C_6H_5(CH_2)_nCH=CH_2$ and $C_6H_5(CH_2)_nCH=C(CH_3)_2$ toward addition by the trichloromethyl radical reaches a maximum when $n = 2$ and decreases as n increases. This dependence of reactivity on chain length is interpreted in terms of a mechanism in which the trichloromethyl radical first complexes with the benzene ring of the phenylalkene, followed by an addition step in which the complexed radical adds to the side chain of the complexing molecule. Nuclear magnetic resonance spectra of the ω -phenyl-2-methyl-2-alkenes also support the importance of conformations in which the side chain bends back, placing certain atoms over the benzene ring for the compounds in which n is 2 or 3.

Introduction

In the preceding paper,² it was postulated that the addition of a trichloromethyl radical to 3-phenyl-

1-propene or 4-phenyl-1-butene proceeded by the initial formation of a π -complex between the aromatic ring of the phenylalkene and the trichloromethyl radical, followed by addition, within the complex, of the

(1) Petroleum Research Fund Predoctoral Fellow, 1961-1962 and 1962-1963.

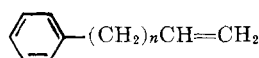
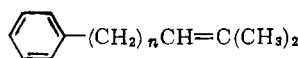
(2) M. M. Martin and G. J. Gleicher, *J. Am. Chem. Soc.*, **86**, 233 (1964).

trichloromethyl radical to the double bond of the side chain attached to the complexing ring. It was pointed out that the experimentally observed ratio of relative rate constants for the disappearance by addition of two phenylalkenes would be given by the expression

$$\left(\frac{k_1}{k_2}\right)_{\text{disappearance by addition}} = \frac{K_1 k_1'}{K_2 k_2'}$$

where K_1 and K_2 are the equilibrium constants for complexation of the trichloromethyl radical with the aromatic rings of the two substrates, and k_1' and k_2' are the specific rate constants for the addition of the complexed radical to the double bond of the side chain of the complexing molecule, a process hereafter referred to as intramolecular addition. In any series of ring-substituted phenylalkenes having the same double-bond-containing side chain, the effect of the substituents will be to modify K_1 and K_2 and thereby be manifested in the different rates at which the two materials are consumed. Such a situation is reported in the previous paper.² On the other hand, compounds which are similarly substituted in the benzene ring, but which possess different side chains, would be expected to exhibit differences in reactivity toward the trichloromethyl radical as a consequence of differences in k_1' and k_2' . This is because ease and probability of near approach by the double bond of the side chain to the complexed trichloromethyl radical will depend upon the nature of the carbon chain separating the double bond from the benzene ring (Fig. 1), thereby influencing the rate of intramolecular addition.

In this paper, the reactions of series of ω -phenyl-1-alkenes (I, $n = 1-6$) and ω -phenyl-2-methyl-2-alkenes (II, $n = 1-6$) with the trichloromethyl radical have been studied.

I, $n = 1-6$ II, $n = 1-6$

In these series, the substitution of the ring is electronically equivalent throughout, so that the equilibrium constants for complexation should all be the same (unless some kind of sandwiched radical, involving complexation by the double bond as well as the phenyl group leading to a more stable complex, is possible in some cases), whereas the position of the double bond relative to the ring varies. If addition does occur within a complex, there should be a dependence of rate of addition on the number of carbon atoms in the chain separating the double bond from the benzene ring. If no complex is formed, or if addition is predominantly intermolecular, no such dependence should be noted, and all the members of any series should react at nearly the same rate.

Experimental

Materials.—The bromotrichloromethane and chlorobenzene were purified as described elsewhere.² The ω -phenyl-1-alkenes are all known compounds and were prepared by the coupling reaction of allyl bromide and an appropriate Grignard reagent.³⁻⁶ The ω -phenyl-2-methyl-2-alkenes were prepared similarly from an alkyl Grignard reagent and 1-chloro-3-methyl-2-butene. Physical properties, yields, and analytical data are presented in Table I.

All of these compounds exhibited infrared absorption between 1673 and 1677 cm^{-1} , due to the triply substituted double bond, and between 800 and 845 cm^{-1} , due to the carbon-hydrogen out-of-plane deformation ($n = 1$, 845 cm^{-1} ; $n = 2$, 800 cm^{-1} ; $n = 3$, 827 cm^{-1} ; $n = 4$, 809 cm^{-1} ; $n = 5$, 825 cm^{-1} ;

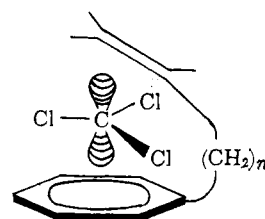


Figure 1.

$n = 6$, 820 cm^{-1}). The n.m.r. spectra, taken on a Varian A-60, confirmed the structures. All exhibited resonance characteristic of the group, $-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)_2$, a triplet due to the vinyl proton between 4.62 and 4.86 τ , and two peaks due to the protons on the allylic methyl groups, between 8.27 and 8.48 τ . Vapor phase chromatography on a 6-ft. 10% diethylene glycol succinate column indicated that all of these compounds are contaminated with about 5% of an isomeric impurity, believed to have the structure $\text{C}_6\text{H}_5-(\text{CH}_2)_n\text{CH}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{CH}_2$, formed by coupling of the Grignard reagent with 2-chloro-2-methyl-3-butene, an impurity present in the 1-chloro-3-methyl-2-butene, or else formed from it during the reaction. Absorp-

TABLE I
 ω -PHENYL-2-METHYL-2-ALKENES

n	Yield, %	B.p., °C.		Formula	Carbon, %		Hydrogen, %	
		mm.	mm.		Calcd.	Found	Calcd.	Found
1	55	85-86	25	$\text{C}_{11}\text{H}_{14}$	90.41	90.20	9.59	9.59
2	35	97-99	25	$\text{C}_{12}\text{H}_{16}$	90.00	89.75	10.00	10.12
3	40	109-111	25	$\text{C}_{13}\text{H}_{18}$	89.59	89.56	10.51	10.42
4	27	121-122	25	$\text{C}_{14}\text{H}_{20}$	89.29	89.22	10.71	10.71
5	24	134-136	25	$\text{C}_{15}\text{H}_{22}$	89.04	89.20	10.96	10.89
6	22	146-148	25	$\text{C}_{16}\text{H}_{24}$	88.82	88.42	11.18	10.86

tion bands around 1650 and 890 cm^{-1} in the infrared, and the presence of an unsplit band at 5.2 τ in an n.m.r. spectrum of a sample enriched in the impurity, suggest the presence of a terminal methylene group and provide the support for the structural assignment.

Procedure for Kinetic Runs. Determination of Relative Rates of Disappearance of Alkenes.—The general procedure was the same as that described elsewhere.² Reactant ratios of bromotrichloromethane: alkene (1):alkene (2):chlorobenzene of from 5:1:1:0.15 to 10:1:1:0.25 were employed. Reactions were run to from 10 to 70% completion. The ratio of rate constants for disappearance of the two olefins was calculated from the expression

$$\left(\frac{k_1}{k_2}\right)_{\text{disapp}} = \frac{\log (\text{moles of 1 initially}/\text{moles of 1 finally})}{\log (\text{moles of 2 initially}/\text{moles of 2 finally})}$$

Analyses were done by vapor phase chromatography as described previously. The ω -phenyl-1-alkenes were studied at 69.5°, the ω -phenyl-2-methyl-2-alkenes at 94.0°. A General Electric 275-w. sunlamp provided ultraviolet irradiation.

Determination of Relative Rates of Addition to Abstraction.—The general procedure was the same as that described elsewhere.² These studies were conducted on the ω -phenyl-2-methyl-2-alkenes only, since measurable quantities of chloroform were not produced from the ω -phenyl-1-alkenes (except in the case of 3-phenyl-1-propene). Reactant mole ratios of bromotrichloromethane: ω -phenyl-2-methyl-2-alkene:chlorobenzene of from 1:6:0.33 to 1:10:0.33 were employed. The reactions were allowed to proceed generally to be-

(3) E. B. Hershberg, *Helv. Chim. Acta*, **17**, 352 (1934).

(4) A. P. Kozacki and E. E. Reid, *J. Am. Chem. Soc.*, **60**, 2436 (1938).

(5) J. von Braun, H. Deutsch, and A. Schmatloch, *Ber.*, **45**, 1246 (1912).

(6) R. Lucas and P. Amagat, *Bull. soc. chim. France*, **51**, 965 (1932).

tween 70 and 100% completion. Ratios of rate constants were independent of initial reactant ratios and extent of reaction. The ratio of the rate constant for addition, k_a , to abstraction, k_t , was calculated from the expression

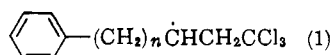
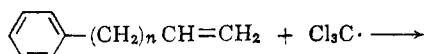
$$\frac{k_a}{k_t} = \frac{\text{moles of BrCCl}_3 \text{ consumed} - \text{moles of HCCl}_3 \text{ formed}}{\text{moles of HCCl}_3 \text{ formed}}$$

In these experiments, small quantities of the isomeric impurity were consumed, but the amounts were so small that the rate constant ratio would not be significantly affected even if all of the impurity which reacted disappeared solely by hydrogen abstraction to produce additional chloroform, or by addition, the more likely alternative, to consume bromotrichloromethane without producing any chloroform.

Calculation of $(k_1/k_2)_{\text{addition}}$ and $(k_1/k_2)_{\text{abstraction}}$.—The ratios $(k_1/k_2)_{\text{addn}}$ and $(k_1/k_2)_{\text{abstn}}$ are readily calculated from $(k_1/k_2)_{\text{disapp}}$ and the (k_a/k_t) ratios for both alkenes, since the rate constant for disappearance is equal to the sum of the rate constants for addition and abstraction for any given compound. For the 1-alkenes, so little abstraction occurred that relative rates of disappearance could be equated with relative rates of addition (except in the case of the lowest member, 3-phenyl-1-propene).

Results

In Table II are indicated the relative rates at which the members of a series of ω -phenyl-1-alkenes disappear by addition of the trichloromethyl radical to the double bond (reaction 1). Only in the case of 3-phenyl-



1-propene ($n = 1$), in which the hydrogens are very labile, could a measurable quantity of chloroform be detected among the products, indicating very high values of k_a/k_t , the minimum measurable value being of the order of 200/1 (a value of 29/1 was observed when $n = 1^2$). The high values of k_a/k_t are in contrast to the value of 43 for 1-octene at 78° ,⁷ and indicate attack by a more selective, less reactive radical. The complexed trichloromethyl radical should be more selective.

TABLE II

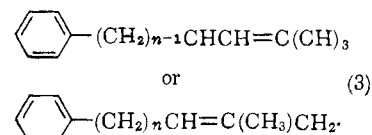
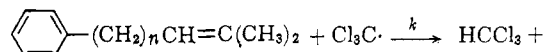
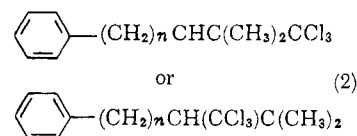
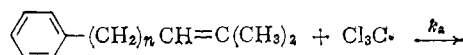
RELATIVE RATE CONSTANTS FOR THE ADDITION OF $\text{Cl}_3\text{C}\cdot$ TO $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{CH}=\text{CH}_2$ AT 69.5°

n	Rel. k	n	Rel. k
1	1.00	4	1.10 ± 0.03
2	1.22 ± 0.04^a	5	$1.00 \pm .02$
3	$1.13 \pm .02$	6	$0.82 \pm .01$

^a Average deviation.

In Table III are the relative rates at which the trichloromethyl radical adds to (reaction 2) and abstracts hydrogens from (reaction 3) a series of ω -phenyl-2-methyl-2-alkenes, the relative rates at which the olefins disappear by both routes, and the ratio k_a/k_t of rate constants of addition to abstraction for each olefin. It should be noted that in both series the rate of addition is a maximum when two carbon atoms separate the double bond and the aromatic ring, and then decreases as the number of carbons in the intervening chain is increased. The magnitude of the decrease is considerably greater in the ω -phenyl-2-methyl-2-alkene series.

(7) E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961).



Discussion

These results support the contention that the addition of the trichloromethyl radical to the double bond of a phenylalkene proceeds *via* initial complexation of the trichloromethyl radical with the aromatic ring, followed by addition to the double bond in the side chain of the complexing aromatic substrate. The rate of addition of the trichloromethyl radical is found to be markedly affected by the relative location of the phenyl group with respect to the double bond, even when the phenyl group is too far removed from the site of addition to exert a direct electronic effect upon its reactivity. The differences in rate of addition reflect the relative tendencies of the side chains of the various molecules to adopt conformations which bring the double bond in the vicinity of the complexed trichloro-

TABLE III

RELATIVE RATE CONSTANTS FOR REACTIONS OF $\text{Cl}_3\text{C}\cdot$ AND $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{CH}=\text{C}(\text{CH}_3)_2$ AT 94.0°

n	Rel. k_a addition	Rel. k_t abstraction	Rel. k_t disappearance	k_a/k_t
1	1.00	1.00	1.00	8.5 ± 0.6^a
2	1.15 ± 0.02^a	0.30 ± 0.01^a	1.06 ± 0.01^a	32.9 ± 1.7
3	$0.57 \pm .01$	$.29 \pm .01$	$0.54 \pm .01$	16.7 ± 1.7
4	$.52 \pm .01$	$.24 \pm .01$	$.49 \pm .01$	18.1 ± 0.5
5	$.38 \pm .01$	$.13 \pm .01$	$.35 \pm .01$	25.4 ± 1.8
6	$.27 \pm .02$	$.08 \pm .01$	$.25 \pm .02$	29.3 ± 2.4

^a Average deviation.

methyl radical, held in the π -cloud of the benzene ring, in spatial arrangements favorable for addition. This is most readily achieved in the lower members of each series when the double bond is separated from the benzene ring by one, two, or three carbon atoms, the two-carbon chain providing an especially favorable situation in that several conformations of the chain bring the double bond close to the site of complexation. As the number of carbons between the ring and the double bond increases, it is still possible for the double bond to come close to the complexed trichloromethyl radical, but an increasingly large number of conformations are possible in which the double bond is held away from the ring. Hence, reactivity toward addition is highest in the lower members of a series when a larger fraction of the available conformations brings the double bond close to the complexed radical, reaching a maximum when two carbon atoms separate the ring and the double bond, then declining as the number of carbon atoms increases. The ponderal effect⁸ would predict a gradual decline in reactivity as chain length increases, as a simple consequence of

(8) C. K. Ingold, *Quart. Rev. (London)*, **11**, 1 (1957). The authors wish to thank a referee for pointing out the pertinence of this effect.

the increased mass of the reacting molecule. This further points out the need for some explanation for a reactivity maximum beyond the first member of the series.

Although the two series of compounds studied both show a reactivity maximum when n is 2, the reactivity sequences of the other members of the series are not identical. Also, the effect is much more pronounced in the ω -phenyl-2-methyl-2-alkenes than in the ω -phenyl-1-alkenes. The differences between the two systems may be a consequence of several factors. First, the high degree of substitution about the double bond in the ω -phenyl-2-methyl-2-alkenes will serve to decrease reactivity in this series, generally.⁷ This will tend to decrease the extent to which intermolecular additions, that is, addition of a complexed trichloromethyl radical to an olefin molecule other than the one serving as the complexing agent, compete with intramolecular additions. Thus the differences in reactivity resulting from the steric factors involved in the intramolecular process will be more manifest in the series involving the heavily substituted double bond than in the series of terminal olefins, in which the indiscriminating intermolecular process tends to swamp out the more selective intramolecular reaction. Also, factors influencing direction of addition differ in the two series. In the ω -phenyl-1-alkenes, addition to the more distant olefinic carbon atom produces the more stable radical (secondary as opposed to primary); whereas in the ω -phenyl-2-methyl-2-alkenes, addition to the more proximate olefinic carbon atom produces the more stable radical (tertiary as opposed to secondary). This difference in preferred direction of addition would render a perfect correlation between the two series highly unlikely.

It is also noteworthy that the relative rate of hydrogen abstraction decreases as the chain length increases. An assessment of the hydrogen abstraction reaction is complicated by the fact that three types of allylic hydrogens—those present on two different methyl groups and the methylene group—as well as a pair of benzylic hydrogens can be abstracted, and the location of all of the labile hydrogens changes relative to the complexed trichloromethyl radical as the side chain is altered. The observed decrease as n increases may suggest the importance of intramolecular abstraction processes in the lower members of the series. However, it is the addition process which is more strongly influenced by proximity of the double bond to the complexed radical.

The credibility of this explanation is enhanced by the n.m.r. spectra of the ω -phenyl-2-methyl-2-alkenes. In Table IV are the chemical shifts of the protons of the terminal allylic methyl groups of these compounds. For comparison, in Table V are the τ -values for the protons of the terminal allylic methyl group of a related series of *trans*- ω -phenyl-2-alkenes. It has been observed^{9,10} that the protons of the methyl groups of a terminal isopropylidene group ordinarily have τ -values of 8.31 and 8.38, the low-field resonance being due to the protons on the methyl group *trans* to the alkyl chain. From these studies^{9,10} and the data recorded in Tables

IV and V, it is apparent that the protons of the methyl group *trans* to the phenylalkyl chain in the ω -phenyl-2-methyl-2-alkenes are associated with normal τ -values of 8.30 to 8.32 (8.27 for the first member of the series), but that in the case of the compounds in which n is 2 or 3, the methyl groups *cis* to the phenylalkyl chain, the methyl groups giving rise to the high field signals, have unusually high τ -values of 8.48 and 8.45. The other high-field signals are where they would be expected to be, within 0.03 to 0.05 τ unit of 8.38. The difference in the τ -values for the two methyl groups in such compounds is ordinarily around 0.07, whereas in the compounds in which n is 2 or 3, the increments are 0.17 and 0.14. This added shielding experienced by the *cis*-methyl group in these two compounds is probably a consequence of the fact that it spends a considerable portion of its time over the plane of the benzene ring, in the diamagnetic region of the field resulting from the ring current. A similar explanation is offered for the high τ -value of 9.20 observed for one of the methyl groups in 2-phenylbutane.¹¹ Models are in accord with the statement that the *cis*-methyl group is the one more likely to reside over the benzene ring. Of course, the terminal allylic methyl group, *cis* to the ω -phenylalkyl group, does not occupy a position identical with that which would be occupied by a trichloromethyl radical complexed with the π -cloud of the benzene ring in the process of adding to the double bond of the side chain, but nonetheless these results do support the notion that the carbon atoms of the double bond spend a considerable portion of their time in the vicinity of the region over the benzene ring when the number of carbon atoms between the ring and double bond is small, and proportionately less as the number increases.

TABLE IV
 τ -VALUES FOR TERMINAL ALLYLIC METHYL PROTONS OF
 $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{CH}=\text{C}(\text{CH}_3)_2$

n	Chemical shifts, τ	$\Delta\tau$
1	8.27, 8.33	0.06
2	8.31, 8.48	.17
3	8.31, 8.45	.14
4	8.30, 8.38	.08
5	8.32, 8.41	.09
6	8.31, 8.41	.10

TABLE V
 τ -VALUE FOR TERMINAL ALLYLIC METHYL PROTONS OF *trans*-
 $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{CH}=\text{CHCH}_3$

n	1	2	3	4
τ	8.30	8.35	8.32	8.32

A related phenomenon has been discussed by Cram and Bauer¹² in their studies of the π -complexes of tetracyanoethylene and α,ω -diphenylalkenes.

Acknowledgment.—It is a pleasure to thank the donors of the Petroleum Research Fund for a grant (PRF No. 603-A) administered by the American Chemical Society which financed the greater part of this work.

(9) M. S. Barber, J. B. Davis, L. M. Jackman, and B. C. L. Weedon, *J. Chem. Soc.*, 2870 (1960).

(10) L. M. Jackman and R. H. Wiley, *ibid.*, 2881 (1960).

(11) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 51.

(12) D. J. Cram and R. H. Bauer, *J. Am. Chem. Soc.*, **81**, 5971 (1959).