

ORGANIC AND BIOLOGICAL CHEMISTRY

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The Addition of the Trichloromethyl Radical to Substituted 3-Phenyl-1-propenes and 4-Phenyl-1-butenes

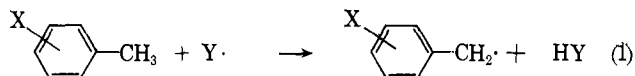
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A Hammett study of the addition of the trichloromethyl radical to 3-phenyl-1-propenes and 4-phenyl-1-butenes has led to ρ -values of -0.29 and -0.20 , respectively. These unexpectedly high values for reactions which produce alkyl radicals insulated from the substituted phenyl group by one and two methylene groups are explained as being the result of the formation of, and intramolecular addition within, a π -complex of the trichloromethyl radical with the phenyl group of the ω -phenyl-1-alkene.

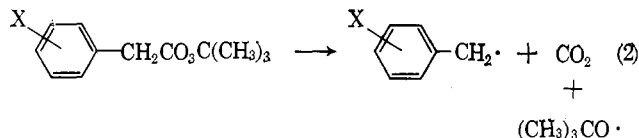
Introduction

Although free radicals are neutral species in a formal sense, it has long been recognized that polar substituents in a molecule can have a considerable effect upon the rate and course of a free radical reaction. Numerous studies²⁻⁷ of hydrogen abstraction reactions from substituted toluenes (reaction 1) and cumenes have provided very useful information on the polar effects

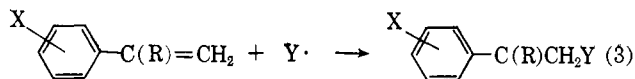


operating in homolytic processes. A summary of published Hammett $\sigma\rho$ correlations involving hydrogen abstraction reactions, including the results of several unpublished investigations, has recently appeared.⁸ The ρ -values for abstraction of a benzylic hydrogen are negative, and correlation is generally better using the electrophilic σ^+ -values than the normal σ -values.

Benzyl radicals have also been generated by the one-step decarboxylation of a series of substituted *t*-butyl phenylperacetates⁹ (reaction 2).



The data correlate better with σ^+ than σ , and lead to ρ -values of -1.04 at 100° and -1.20 at 56° . Studies of free radical addition reactions to styrenic compounds to produce benzyl radicals (reaction 3) have

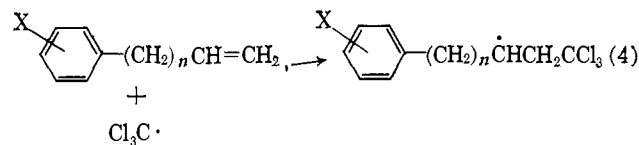


not led to very linear Hammett correlations, but acceleration by electron-supplying groups is apparent in all cases in which the attacking radical is electrophilic.¹⁰

The precise origin of these polar effects is a matter of current interest, and two explanations have been advanced,¹⁰⁻¹³ but the established fact is that electron-

donating groups tend to accelerate and electron-withdrawing groups decelerate homolytic processes in which a benzyl radical is generated by the reaction of an aromatic substrate with an electrophilic radical.

In this paper the polar effects operating in reactions in which a radical carbon atom is generated two or three carbon atoms removed from the substituted phenyl group are reported. Since the radical carbon atom so generated is insulated from the substituted phenyl group by one or two methylene groups, the influence of the substituent would be expected to be slight. The reaction chosen for study was the addition of the trichloromethyl radical, generated from bromotrifluoromethane, to series of substituted 3-phenyl-1-propenes (Ia) and 4-phenyl-1-butenes (Ib) (reaction 4).

Ia, $n = 1$; b, $n = 2$

Experimental

Materials. Bromotrifluoromethane (Matheson Coleman and Bell) was distilled through a 30-in. helices-packed column, taking only a middle cut, b.p. $103-103.5^\circ$. This distilled portion was washed with water, dried with sodium sulfate, and redistilled at reduced pressure, b.p. 43° (80 mm.). Gas phase chromatography on a 15-ft. 10% silicone gum rubber column indicated that the material was 99.2% pure. The impurity had the same retention time as carbon tetrachloride and a different retention time from chloroform.

Chlorobenzene (Eastman) was shaken with three portions of sulfuric acid, once with water, three times with 5% sodium bicarbonate, again with water, dried successively over calcium chloride, calcium sulfate, and phosphorus pentoxide, and distilled; b.p. $130-130.5^\circ$.

The 3-phenyl-1-propenes and 4-phenyl-1-butenes were prepared by the coupling reaction of allyl bromide with the appropriate phenylmagnesium bromide¹⁴ or benzylmagnesium chloride.¹⁵ 4-(4-Methoxyphenyl)-1-butene was prepared by the reverse process, that is, from allylmagnesium bromide and *p*-methoxybenzyl chloride. Coupling of *p*-methoxybenzylmagnesium chloride with allyl bromide gave only a 5% yield of 4-(4-methoxyphenyl)-1-butene, leading mainly to 4,4'-dimethoxybibenzyl. Yields, boiling points, and analytical data on all new compounds are presented in Table I (3-phenyl-1-propenes) and Table II (4-phenyl-1-butenes). All of these compounds were purified by distillation and were adjudged pure when gas phase chromatography on a diethylene glycol succinate column resulted in only one peak. In some instances, the initially distilled 4-phenyl-1-butenes contained traces of unreacted benzyl chloride. This was removed by heating the liquid product with triethyl-

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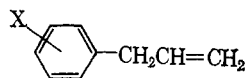
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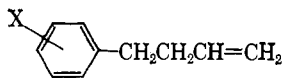
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TABLE I
 SUBSTITUTED 3-PHENYL-1-PROPENES


X	Yield, %	B.p., °C.	Formula	Carbon, %		Hydrogen, %		Other, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
H	76	153-154 ^a	C ₉ H ₁₀
<i>p</i> -CH ₃	61	180-183 ^b	C ₁₀ H ₁₂
<i>m</i> -CH ₃	60	180-183 ^c	C ₁₀ H ₁₂
<i>p</i> -Cl	74	199-201	C ₉ H ₉ Cl	70.83	70.81	5.94	6.00	23.23	23.40
<i>m</i> -Cl	70	198-202	C ₉ H ₉ Cl	70.83	70.70	5.94	5.91	23.23	23.10
<i>p</i> -CH ₃ O	67	213-216 ^d	C ₁₀ H ₁₂ O
<i>m</i> -CH ₃ O	50	213-216	C ₁₀ H ₁₂ O	81.08	81.09	8.11	8.29
<i>p</i> -C ₆ H ₅	55	132-135 (1 mm.)	C ₁₅ H ₁₄	92.74	92.71	7.26	7.42
<i>p</i> -F	47	157-160	C ₉ H ₉ F	79.42	79.39	6.70	6.66	14.08	13.95
<i>p</i> -CF ₃	60	168-171	C ₁₀ H ₉ F ₃	64.51	64.36	4.85	4.93	30.64	30.46
<i>m</i> -CF ₃	52	164-166	C ₁₀ H ₉ F ₃	64.51	64.39	4.85	4.97	30.64	30.50

^a Lit.¹⁴ 153-154°. ^b Lit. 180-181°, ¹⁶ 180-182°. ¹⁷ ^c Lit.¹⁷ 60° (11 mm.). ^d Lit.¹⁸ 215-216°.

 TABLE II
 4-PHENYL-1-BUTENES


X	Yield, %	B.p.		Formula	Carbon, %		Hydrogen, %		Other, %	
		°C.	mm.		Calcd.	Found	Calcd.	Found	Calcd.	Found
H	70	176.5-177 ^a		C ₁₀ H ₁₂
<i>p</i> -CH ₃	42	83	12	C ₁₁ H ₁₄	90.33	90.36	9.67	9.77
<i>m</i> -CH ₃	58	91-92	20	C ₁₁ H ₁₄	90.33	90.19	9.67	9.50
<i>p</i> -Cl	68	93-93.5	10	C ₁₀ H ₁₁ Cl	72.08	72.13	6.66	6.73	21.28	21.12
<i>m</i> -Cl	76	91-92	12	C ₁₀ H ₁₁ Cl	72.08	72.21	6.66	6.70	21.28	21.50
<i>p</i> -F	64	85-86	30	C ₁₀ H ₁₁ F	79.95	79.97	7.40	7.53	12.65	12.77
<i>m</i> -F	59	76-77	20	C ₁₀ H ₁₁ F	79.95	80.07	7.40	7.52	12.65	12.50
<i>p</i> -CH ₃ O	26	110.5-111	14	C ₁₁ H ₁₄ O	81.44	81.35	8.70	8.44
<i>m</i> -CH ₃ O	45	105-106	12	C ₁₁ H ₁₄ O	81.44	81.46	8.70	8.90

^a Lit.¹⁵ b.p. 181-182°.

amine for 10 hr. at 85°, then washing with water and dilute hydrochloric acid, drying, and distilling the residue. The absence of any benzyl chloride was confirmed by v.p.c. and by testing for active halogen with alcoholic silver nitrate solution. All of these olefins exhibited an infrared maximum between 1640 and 1653 cm.⁻¹, characteristic of an unconjugated double bond, and a maximum between 905 and 925 cm.⁻¹ and one between 985 and 1000 cm.⁻¹, characteristic of a terminal vinyl group. No bands attributable to compounds in which the double bond had rearranged by migration into conjugation with the benzene ring were evident. The ultraviolet spectra also indicated the presence of a substituted phenyl group, unconjugated with the double bond of the side chain. These compounds are definitely not contaminated with any styrenic products.

Products.—A mixture of 1.197 g. (0.0101 mole) of 3-phenyl-1-propene and 8.729 g. (0.0443 mole) of bromotrichloromethane, sealed under nitrogen in a Pyrex ampoule, was placed in a horizontal position just beneath the surface of an oil bath maintained at 69.5 ± 0.2°, and irradiated for 19 hr. by a General Electric 275-w. sunlamp placed 19 cm. from the surface. At the end of this time, v.p.c. analysis on a diethylene glycol succinate column indicated complete utilization of the 3-phenyl-1-propene. Excess bromotrichloromethane was removed by heating on a steam bath at aspirator pressure, after which there remained 3.04 g. of a transparent brown residue, consisting of the 1:1 adduct, 1,1,1-trichloro-3-bromo-4-phenylbutane, and the bromination product, 3-bromo-1-phenylpropene. Making use of the ratio for the rate of addition of the trichloromethyl radical to the double bond to the rate of abstraction by the trichloromethyl radical of a labile hydrogen atom, determined as described below, it can be calculated that this corresponds to a yield of 2.93 g. (93.8%) of 1:1 adduct, and 0.11 g. (3.3%) of bromination product. Extensive decomposition and fuming occurred when this residue was distilled, so that purification of the entire sample was not achieved. The physical properties of a sample of distillate agreed satisfac-

torily with those reported for the adduct by Kharasch and Sage¹⁹, b.p. 178° (30 mm.), *n*_D²⁰ 1.5640 (lit.¹⁹ b.p. 79° (0.05 mm.), *n*_D²⁰ 1.5650).

The mode of addition was established as follows. A mixture of 6.91 g. (0.022 mole) of adduct and 3.57 g. (0.044 mole) of lithium aluminum hydride in 50 ml. of ether was refluxed for 2 days. The reaction mixture was hydrolyzed by the addition of 3.6 g. of water and 5.3 g. of 10% sodium hydroxide solution, the mixture filtered, layers separated, and the ether layer was dried. The product was analyzed by v.p.c. at 120° on a 10% diethylene glycol succinate column. The major product peak corresponded to *n*-butylbenzene. No peak corresponding to isobutylbenzene was present. From a consideration of the minimum quantity of isobutylbenzene that could have been detected, it was concluded that at least 99% of the addition occurred at the terminal position.

In a similar experiment, 6.62 g. (0.05 mole) of 4-phenyl-1-butene and 20 g. (0.10 mole) of bromotrichloromethane were irradiated for 27 hr. at 69.5 ± 0.2°. All of the 4-phenyl-1-butene was found to have reacted, and excess bromotrichloromethane was removed by heating the reaction mixture at 80° and 0.2 mm. for 3 hr. The transparent, light brown residue weighed 16.0 g., corresponding to a 97% yield of 1:1 adduct. This liquid could be distilled with some decomposition, b.p. 122° (0.35 mm.). The infrared spectrum showed characteristic aromatic absorption of the type expected of a monosubstituted benzene, although the bands due to carbon-chlorine obscure this region to some extent. No bands attributable to a double bond were present.

Anal. Calcd. for C₁₁H₁₂BrCl₃: C, 39.96; H, 3.66; Br, 24.17; Cl, 32.17. Found: C, 40.05; H, 3.71; Br, 24.18; Cl, 32.22.

Determination of Relative Rates of Addition to Abstraction.—Samples of the olefin and a stock mixture of bromotrichloromethane and chlorobenzene were accurately weighed into an amber vial. The weights used corresponded to mole ratios of olefin:bromotrichloromethane:chlorobenzene of 8:2:1. The olefin was used in excess so that the favored reaction of the trichloromethyl radical would be with olefin and not with bromo-

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trichloromethane or a product of the reaction. Chlorobenzene served as an inert standard in the v.p.c. analyses. A sample of this solution was sealed under an atmosphere of nitrogen in a Pyrex ampoule, and placed horizontally just beneath the surface of an oil bath maintained at $69.5 \pm 0.2^\circ$, and irradiated by a General Electric 275-w. sunlamp placed 19 cm. from the surface. The extent of reaction, that is, the per cent of bromotrichloromethane consumed during a given time of irradiation, was not a very reproducible quantity, since the chain process by which bromotrichloromethane adds to olefins is quite susceptible to trace impurities which can serve as initiators, promoters, retarders, and inhibitors. In these studies, the ampoule was irradiated such that from 15 to 90% of the bromotrichloromethane was consumed. The ratio of rate constants for addition to abstraction was independent of the extent of reaction. Reactions were run in duplicate, and in some cases triplicate and quadruplicate. The ratio of k_a/k_t was calculated from the expression

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

where k_a is the rate constant for addition (reaction 4) and k_t is the rate constant for abstraction of a labile hydrogen. Analyses were conducted in duplicate or triplicate by gas phase chromatography (v.p.c.) on a 6-ft. 10% diethylene glycol succinate column (LAC-728). Relative areas under curves were determined with the aid of a disk integrator.

In general it was observed that in experiments in which k_a/k_t ratios were determined for the 3-phenyl-1-propenes, more olefin was consumed than bromotrichloromethane. This is most likely a result of reactions between the alkyl radical produced by reaction of the trichloromethyl radical and the 3-phenyl-1-propene with other olefin molecules, such as polymerization (reaction 5) or hydrogen abstraction (reaction 6). Such a reaction sequence would require the consumption of more olefin than bromotrichloromethane, and is very reasonable in a medium in which olefin is present in a fourfold excess over bromotrichloromethane. It does not invalidate the calculations of k_a/k_t since it provides no alternative modes of consumption of bromotrichloromethane or formation of chloroform.

With the 4-phenyl-1-butenes, no chloroform could be detected in the irradiated mixtures of reactions carried out as described above. Thus, accurate k_a/k_t ratios could not be calculated. Minimum values of the order of 200/1 can be estimated from the limits of the experimental method. The real values are probably much higher. With the 4-phenyl-1-butenes, the number of moles of bromotrichloromethane and olefin consumed were generally within 5% of each other, indicating much longer chains than in the reaction involving 3-phenyl-1-propenes and less reaction of intermediate alkyl radicals with olefin.

Determination of Rates of Disappearance of Substituted Relative to Unsubstituted ω -Phenyl-1-alkenes.—Samples were prepared and irradiations conducted in the same way as described for the determination of k_a/k_t . Mole ratios of substituted olefin: unsubstituted olefin: bromotrichloromethane: chlorobenzene were 1:1:4:0.1 in the case of the 3-phenyl-1-propenes and 1:1:8:0.2 in the case of the 4-phenyl-1-butenes. Bromotrichloromethane was used in excess to favor chain propagation by reaction of the alkyl radical produced in the addition or abstraction step with bromotrichloromethane and to suppress polymerization or termination involving abstraction of a hydrogen from olefin, that is, reactions of the type depicted in 5 and 6.

Relative rates of disappearance of the two olefins by all reaction paths was calculated from the expression

$$k_X/k_H = \log X_i/X_f / \log H_i/H_f$$

where k_X is the rate constant for disappearance of the substituted compound, k_H the rate constant for the unsubstituted compound, X_i and H_i the initial numbers of moles of substituted and unsubstituted olefin, respectively, and X_f and H_f the final numbers of moles of substituted and unsubstituted olefin, respectively. Analyses were conducted by v.p.c. on a 6-ft. 10% diethylene glycol succinate column. The fluoro compounds were not completely separated from the unsubstituted compounds on v.p.c., and in those cases competitive experiments involving the fluoro compound and a methyl or chloro compound were run. Then, k_F/k_H was calculated from an expression such as

$$k_F/k_H = k_F/k_{CH_3} \times k_{CH_3}/k_H$$

The analyses were not conducted in such a manner which gave high precision to the measurement of the area of the bromotrichloromethane peak. This material came off the column very rapidly, giving a spike-like peak. However, in several instances in which the number of moles of bromotrichloromethane consumed was carefully determined, it was found that it was very close to the total number of moles of olefin consumed, confirming that the olefin is being consumed only in the formation of 1:1 adduct and is not disappearing by polymerization.

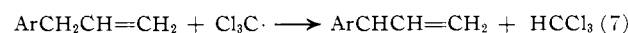
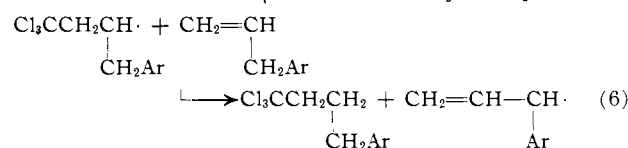
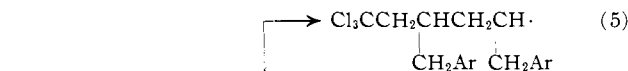
Calculations.—The rate constant ratios, k_X/k_H for addition and abstraction are readily calculated, since the experimentally

determined rate constant for disappearance is equal to the sum of the rate constants for addition and abstraction, that is, $k = k_a + k_t$, and k_a/k_t is known for each individual compound. Since abstraction was negligible with the 4-phenyl-1-butenes, the measured k_X/k_H ratio for disappearance is equal to the ratio for addition.

The Hammett ρ -values were calculated from least squares plots of $\log k_X/k_H$ vs. σ° , according to the procedure recommended by Taft.²⁰⁻²² The σ° -constant reflects all polar effects exerted by a substituent, both inductive and mesomeric, which are ultimately transmitted to the reaction center by induction, and excludes polar effects resulting from direct resonance interactions between substituent and reaction center. The correlation coefficients were calculated according to standard statistical methods.²³

Results

Course of the Reaction.—In any kinetic study in which the disappearance of a compound is followed, it must be established with certainty that the substance is disappearing by the reaction which the investigator claims to be studying. In the case of the disappearance of ω -phenylalkenes upon reaction with trichloromethyl radicals, several paths other than addition to the terminal vinyl group are conceivable: (a) addition to the ring, (b) polymerization (reaction 5) or termination (reaction 6) involving the olefin, and (c) abstraction of a labile hydrogen by the trichloromethyl radical (reaction 7).



A survey of the literature indicates that ring addition (a) can be ruled out as a complicating reaction. The synthetic aspects of the addition of bromotrichloromethane to olefins has been extensively studied,^{19,24-26} and it has been found to proceed much more readily than the much slower attack on an aromatic system.^{27,28}

Polymerization (b) can be ruled out on several grounds. The high yields of 1:1 product (adduct plus bromination product), 97% from both 3-phenyl-1-propene and 4-phenyl-1-butene, is a good indication that olefin is not being consumed by polymerization or termination as depicted in reactions 5 and 6. Also, in several of the kinetic runs in which the number of moles of bromotrichloromethane consumed was carefully determined, it was found that the total number of moles of olefin consumed corresponded very closely to the total number of moles of bromotrichloromethane consumed.

The failure to detect any chloroform in the reactions of bromotrichloromethane with the 4-phenyl-1-butenes rules out abstraction of a labile hydrogen atom as a complication. Small quantities of chloroform were detected in the 3-phenyl-1-propene series, and a ratio of the rate constant for addition, k_a , to the rate con-

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TABLE III

RELATIVE RATES OF ADDITION TO ABSTRACTION IN THE REACTION OF $\text{XC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$ WITH $\text{Cl}_3\text{C}\cdot$ AT 69.5°

Substituent	k_a/k_t	Substituent	k_a/k_t
<i>p</i> -CH ₃ O	23.8 ± 1.5 ^a	<i>m</i> -CH ₃ O	32.5 ± 0.03
<i>p</i> -CH ₃	25.3 ± 0.3	<i>p</i> -Cl	32.9 ± 1.1
<i>m</i> -CH ₃	28.5 ± 1.9	<i>m</i> -Cl	40.1 ± 0.85
H	28.9 ± 1.0	<i>m</i> -CF ₃	42.9 ± 1.6
<i>p</i> -C ₆ H ₅	29.1 ± 1.7	<i>p</i> -CF ₃	44.9 ± 1.9
<i>p</i> -F	30.3 ± 1.0		

^a Average deviation.

stant for hydrogen abstraction, k_t , was determined for each compound. The results are summarized in Table III.

These values of k_a/k_t ranging from 24 to 45 for the 3-phenyl-1-propenes and in excess of 200 for the 4-phenyl-1-butenes are unexpectedly high. Huyser²⁹ observed a k_a/k_t ratio of 43 for 1-octene at 77.8° . Considering that 4-phenyl-1-butene contains benzylic as well as allylic hydrogens, a value of k_a/k_t of 200 is unexpectedly large. Also, considering the great lability of the aliphatic hydrogens in 3-phenyl-1-propene, values of k_a/k_t less than 24 would have been expected. 3-Phenyl-1-propene, 4-phenyl-1-butene, and 5-phenyl-1-pentene have all been observed to form unexpectedly high molecular weight alternating copolymers with maleic anhydride,³⁰ also pointing to a high rate of addition relative to hydrogen abstraction.

Data in the literature^{24-26,29} indicate that the addition of the trichloromethyl radical to a terminal olefin is practically entirely, if not exclusively, at the terminal position. In this work, it was confirmed that terminal addition was favored over nonterminal addition in the case of 3-phenyl-1-propene, by a factor of 99:1. Thus, it is concluded that the rate of disappearance of olefin in these reactions is a measure of the rate of addition to the terminal position of the double bond (reaction 4), with a small correction for hydrogen abstraction from the 3-phenyl-1-propenes.

Relative Rates of Addition.—In Table IV are presented the rates of addition of trichloromethyl radicals to substituted 3-phenyl-1-propenes, relative to the unsubstituted compound, and the relative rates of hydrogen abstraction by trichloromethyl from these compounds. In Table V are the relative rates of addition to the series of 4-phenyl-1-butenes. Negligible abstraction was observed.

TABLE IV

RELATIVE RATES OF ADDITION AND ABSTRACTION IN THE REACTION

 $\text{XC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2 + \text{Cl}_3\text{C}\cdot$ AT 69.5°

Substituent	σ^{21}	(k_X/k_H) , addition	(k_X/k_H) , abstraction
<i>p</i> -CH ₂ O	-0.16	1.20 ± 0.06 ^a	1.46 ± 0.07 ^a
<i>p</i> -CH ₃	-0.15	1.24 ± .02	1.42 ± .03
<i>m</i> -CH ₃	-0.07	1.13 ± .04	1.15 ± .04
H	.00	1.000	1.000
<i>p</i> -C ₆ H ₅	.00	1.02 ± 0.08	1.02 ± 0.08
<i>m</i> -CH ₃ O	+0.13	0.93 ± .01	0.82 ± .01
<i>p</i> -F	+0.17	.99 ± .04	.94 ± .03
<i>p</i> -Cl	+0.27	.88 ± .05	.78 ± .05
<i>m</i> -Cl	+0.37	.86 ± .02	.60 ± .01
<i>m</i> -CF ₃	+0.42 ^b	.80 ± .03	.54 ± .02
<i>p</i> -CF ₃	+0.55 ^b	.73 ± .02	.47 ± .01

^a Average deviation. ^b σ° -values for *m*- and *p*-CF₃ are not available, but for strongly electron-withdrawing groups, $\sigma \approx \sigma^\circ$. The values used were σ -values.³¹

(29) E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961).(30) M. M. Martin and N. P. Jensen, *ibid.*, **27**, 1201 (1962).

(31) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 72.

TABLE V

RELATIVE RATES OF ADDITION IN THE REACTION $\text{XC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2 + \text{Cl}_3\text{C}\cdot$ AT 69.5°

Substituent	σ^{21}	(k_X/k_H) , addition
<i>p</i> -CH ₃ O	-0.16	1.07 ± 0.05 ^a
<i>p</i> -CH ₃	-0.15	1.10 ± .02
<i>m</i> -CH ₃	-0.07	1.08 ± .01
H	.00	1.000
<i>m</i> -CH ₃ O	+0.13	0.96 ± 0.04
<i>p</i> -F	+0.17	.94 ± .06
<i>p</i> -Cl	+0.27	.88 ± .02
<i>m</i> -F	+0.35	.90 ± .02
<i>m</i> -Cl	+0.37	.84 ± .04

^a Average deviation.

In Table VI the Hammett ρ -values are recorded. In Fig. 1 and 2 the graphical plots of $\log(k_X/k_H)$ for addition *vs.* σ° are represented.

TABLE VI

HAMMETT ρ -VALUES

Reaction (69.5°)	ρ	r^a
Addition of $\text{Cl}_3\text{C}\cdot$ to $\text{XC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$	-0.29 ± 0.02 ^c	-0.98
Addition of $\text{Cl}_3\text{C}\cdot$ to $\text{XC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	-0.20 ± .02 ^c	-0.97
Abstraction of H by $\text{Cl}_3\text{C}\cdot$ from $\text{XC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2^b$	-0.58 ± .02	-0.99

^a Correlation coefficient. ^b Calculated according to the procedure recommended by Taft,¹⁹⁻²¹ in which the ρ -value is calculated from the points corresponding to *m*-CH₃, H, *m*-CH₃O, *m*-Cl, *m*-CF₃, and *p*-CF₃. The other points, corresponding to *p*-CH₃O, *p*-CH₃, *p*-F, *p*-C₆H₅, and *p*-Cl, are capable of direct resonance interaction with the radical center adjacent to the phenyl group. The deviations exhibited by these points indicate that such a resonance effect is significant. The calculated R -values are: *p*-CH₃O (+0.31); *p*-CH₃ (+0.12); *p*-C₆H₅ (+0.07); *p*-F (+0.28); *p*-Cl (+0.16). ^c The ρ -values, calculated using ordinary Hammett σ -values are -0.28 ($r = -0.97$) for the 3-phenyl-1-propenes and -0.18 ($r = -0.96$) for the 4-phenyl-1-butenes. The use of σ^+ -values is not appropriate since there is no direct resonance interaction between substituent and reaction center.

The ρ -value for hydrogen abstraction by trichloromethyl radicals from toluenes is -1.46,⁵ considerably higher than the -0.58 observed for the allylbenzenes. This is as it should be, since the abstraction of a hydrogen atom from a 3-phenyl-1-propene is a lower energy process than from a toluene, as a result of the greater stability of an α -vinylbenzyl free radical compared to a benzyl radical. This compression of the energy scale results in a corresponding diminution of the effects of a substituent in the ring.

Discussion

In common with the other Hammett correlations discussed in the Introduction,²⁻¹⁰ negative ρ -values were observed for the addition of the trichloromethyl radical to 3-phenyl-1-propenes ($\rho = -0.29$) and 4-phenyl-1-propenes ($\rho = -0.20$). However, these ρ -values seem rather large for homolytic reactions of relatively low activation energy which produce radical centers two and three carbon atoms distant from the substituted phenyl group. A ρ -value probably no greater than -0.1 would be expected for the addition of the trichloromethyl radical to the 3-phenyl-1-propenes on the basis of the following considerations. If two reactions series involve species of comparable polarity, that reaction series associated with the lower activation energy will be characterized by the ρ -value of lower absolute magnitude. Thus the ρ -value for hydrogen abstraction by the benzylperoxy radical from toluene is -0.705 and from cumene is -0.375.^{3,8} The ρ -value for hydrogen abstraction by the trichloromethyl radical from toluene is -1.46⁵ and from 3-phenyl-1-propene

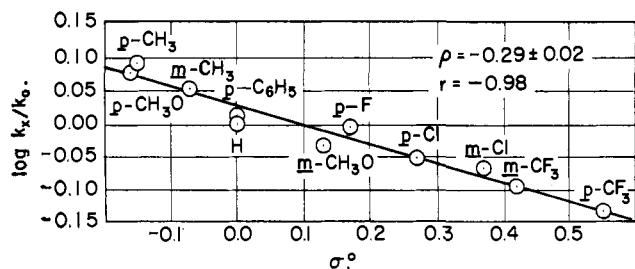


Fig. 1.—Correlation of $\log k_X/k_0$ and σ° for the addition of $\text{Cl}_3\text{C}\cdot$ to $\text{XC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$.

is -0.58 , and for abstraction by the bromine atom is -1.39 for toluene⁷ and -0.76 for 3-phenyl-1-propene.³² The ρ -value for abstraction of a hydrogen atom from toluene by a bromine atom is -1.39^7 and by a chlorine atom is -0.66 .^{4,8} Temperature differences among the various studies cited complicates direct comparison of the ρ -values reported, but there can be no doubt that in each case the reaction series involving the production of the more stable radical type (cumyl *vs.* benzyl, α -vinylbenzyl *vs.* benzyl) or the one involving the more reactive atom (chlorine *vs.* bromine), that is, the reaction series of lower activation energy, is associated with a lower ρ -value. Now, the high values of the ratios of rate constants of addition to abstraction (24 to 45) observed for the 3-phenyl-1-propenes indicates that the addition of a trichloromethyl radical to the terminal double bond has a lower activation energy than abstraction of a benzylic hydrogen atom. Consequently, the ρ -value for addition would be expected to be less than the ρ -value for the abstraction reaction. The exact magnitude of this difference is difficult to specify, but a factor of two or three would seem reasonable. However, in addition to these features of the comparative energetics of the two processes, the addition reaction produces a radical center one carbon atom further distant from the substituted phenyl group than does the abstraction reaction, which will reduce the ρ -value by another factor of about 2.5.^{33,34} Thus, from these considerations, a ρ -value roughly of the order of one-sixth to one-ninth that of hydrogen abstraction from 3-phenyl-1-propenes by the trichloromethyl radical (-0.58) would be anticipated for the addition of the trichloromethyl radical to the terminal double bond of the 3-phenyl-1-propenes. Thus, a maximum value of -0.1 would be expected for addition to the 3-phenyl-1-propenes and of -0.05 for addition to the 4-phenyl-1-butenes.

Several explanations for the origin and mode of transmission of the observed effects must be considered. One possibility is that the formation of bridged radicals, analogous to phenonium ions,³⁵ could result in resonance stabilization of the β -phenylethyl and γ -phenylpropyl radicals formed by the addition of trichloromethyl radicals to 3-phenyl-1-propenes and 4-phenyl-1-butenes. However, other studies³⁶⁻³⁸ have shown that such nonclassical radicals are not formed. Also, the excellent correlation with σ° without deviations by strongly electron-donating groups argues against a direct resonance effect. Neither does a pure inductive effect, operating through the intervening methylene groups, seem to be a satisfactory explanation for the observed polar effect. As has already been

(32) M. M. Martin and G. J. Gleicher, *J. Org. Chem.*, **28**, 3266 (1963).

(33) H. Jaffé, *Chem. Rev.*, **53**, 216 (1953).

(34) M. M. Martin and G. J. Gleicher, *J. Am. Chem. Soc.*, **86**, 242 (1964).

(35) See E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 575, for lead references.

(36) F. H. Seubold, *J. Am. Chem. Soc.*, **75**, 2532 (1953).

(37) C. G. Overberger and H. Gainer, *ibid.*, **80**, 4561 (1958).

(38) M. M. Martin, *ibid.*, **84**, 1986 (1962).

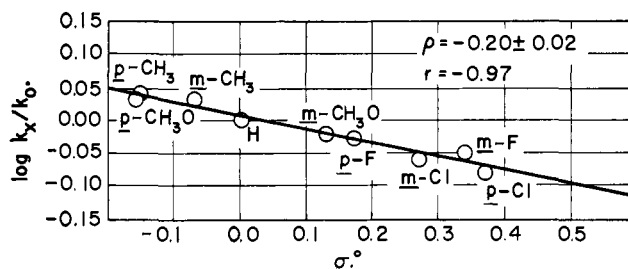
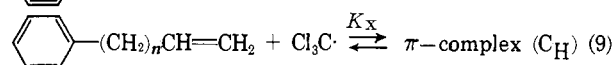
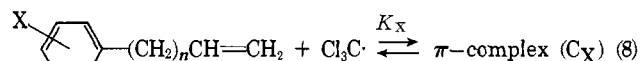


Fig. 2.—Correlation of $\log k_X/k_0$ and σ° for the addition of $\text{Cl}_3\text{C}\cdot$ to $\text{XC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$.

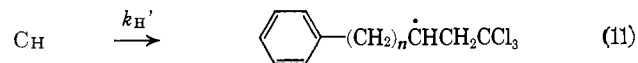
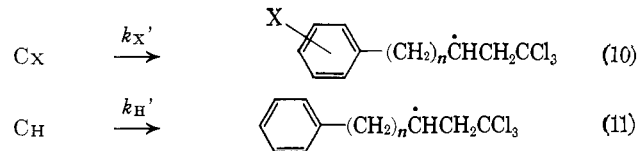
pointed out, the magnitudes of the ρ -values seem too large to be explained on such a basis, and in any case, there should be a larger decrease in the σ -value for addition to 4-phenyl-1-butene from the value for the addition to 3-phenyl-1-propene than is observed, since an additional methylene group is interposed between the benzene ring and the reaction center. Nor does a field effect, operating through space, provide an adequate explanation, since as will be pointed out in the next paper,³⁹ the double bond of the 4-phenyl-1-butene series comes much closer to the phenyl group than does the double bond of the 3-phenyl-1-propene series. Hence, polar effects would be transmitted more efficiently to the reaction site in the 4-phenyl-1-butenes, and the 4-phenyl-1-butenes would have the ρ -value of greater magnitude.

We would like to suggest that the formation of π -complexes provides a satisfactory explanation for these results. The formation of π -complexes between atoms or radicals and aromatic systems has been suggested as an explanation for the effects of aromatic solvents on the selectivity of the chlorine atom in hydrogen abstraction reactions,^{40,41} the effect of aromatics on the reactions of the *t*-butoxy radical,^{42,43} and as intermediates in aromatic halogen interchange reactions.^{44,45} π -Complexes of iodine atoms and aromatic hydrocarbons have also been studied spectrally.⁴⁶ Recently this subject has been discussed with great clarity by Stefani and Szwarc.⁴⁷

It is proposed that the trichloromethyl radicals are complexed by the aromatic substrates in an equilibrium step (reactions 8 and 9) prior to addition to the double bond. The formation of the adduct then proceeds



by intramolecular addition of the trichloromethyl radical to the double bond of the side chain attached to the aromatic group with which it is complexed (reactions 10 and 11). A straightforward treatment of



(39) M. M. Martin and G. J. Gleicher, *ibid.*, **86**, 238 (1964).

(40) G. A. Russell, *ibid.*, **79**, 2977 (1957); **80**, 4987, 4997 (1958).

(41) C. Walling and M. J. Mayahi, *ibid.*, **81**, 1485 (1959).

(42) G. Russell, *J. Org. Chem.*, **24**, 300 (1959).

(43) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

(44) B. Miller and C. Walling, *ibid.*, **79**, 4185 (1957).

(45) B. Milligan, R. L. Bradow, J. C. Rose, H. E. Hubbert, and A. Roe, *ibid.*, **84**, 158 (1962).

(46) R. L. Strong, S. J. Rand, and J. A. Britt, *ibid.*, **82**, 5053 (1960).

(47) A. P. Stefani and M. Szwarc, *ibid.*, **84**, 3661 (1962).

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).