

As mentioned above, there appears to have been no serious attempt to generate 1,2-cyclopentadiene. From our calculations this suggests itself as a fruitful field of study since not only should such species be readily available from the bicyclopentane precursors, but the decrease in the internal bond angle may well be sufficient to cause the drastic change in the electronic structure of the allene moiety suggested by these calculations. If such were the case, the chemical behavior

of this species would be expected to be very much different from that of 1,2-cyclohexadiene.

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Substituent Effects in the Radical Trichloromethylation of 9-X-Anthracenes. An Observed Linear Free Energy Relationship¹

James C. Arnold,^{2a} Gerald Jay Gleicher,* and Jerry D. Unruh^{2b}

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. Received October 17, 1973

Abstract: The reaction rates of the trichloromethyl radical addition to a series of 9-substituted anthracenes relative to *trans*-stilbene have been determined at 70.0°. It is demonstrated here that there is a definite substituent dependence for this addition reaction, and that when the logarithms of the relative rates are plotted *vs.* Brown's σ_p^+ substituent parameters for the 9-X-anthracenes, good correlation is obtained ($r = 0.970$) with $\rho^+ = -0.83$. Significant deviations from this line are observed for two types of compounds. The deviation for compounds such as 9-nitroanthracene is explained in terms of steric inhibition of resonance. Compounds with readily abstractable hydrogen atoms such as 9-methylanthracene tend to undergo appreciable side-chain reaction.

We have reported on the relative reactivities of a series of arylmethanes toward hydrogen atom abstraction by the trichloromethyl radical.^{3,4} The kinetics were shown to exhibit a spread of about three powers of ten for the 13 compounds studied. Not only were the reactivities dependent on the aryl moiety but also were quite dependent on the position of the methyl group; the three methylanthracenes had, for example, a rate spread of about 20. Experimentally it was known, however, that the course of reaction of this series of compounds was not clean. The scope of possible reactions involving addition to the aromatic ring *are outlined* in Scheme I. The magnitude of the radical addition problem was clearly illustrated when a series of arylmethanes was subjected to hydrogen abstraction by bromine atom.⁵ Gilliom and coworkers found that compounds which were anthracene or pyrene derivatives did not afford side-chain bromination but rather a rapid ring substitution reaction. The above considerations served to spur our interest in the reaction of the trichloromethyl radical with aromatic systems.

In an early investigation on the process of radical addition to aromatics, Kooyman and Farenhorst

(1) Presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973.

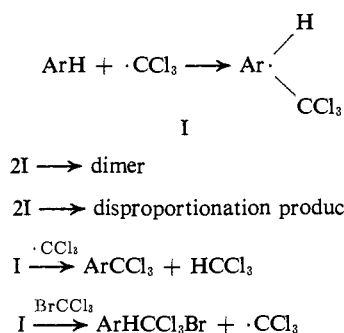
(2) (a) National Defense Education Act Title IV Fellow, 1971–present; (b) National Science Foundation Trainee, 1966–1970.

(3) J. D. Unruh and G. J. Gleicher, *J. Amer. Chem. Soc.*, **91**, 6211 (1969).

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Scheme I. Trichloromethyl Radical Addition to Aromatic Hydrocarbons and Reaction Pathways Available to the Intermediate Radical



studied the addition of trichloromethyl radicals to *n*-hexadecene and styrene.⁶ They found that these reactions were retarded by added aromatic hydrocarbon and from the extent of retardation were able to measure the relative rates of reactivities of the various aromatics toward the trichloromethyl radical. It was found that an approximate linear relationship held between the logarithms of the relative rate constants and the maximum free valencies (F_{max} , as calculated by a Hückel molecular orbital approach) for the respective aromatic compounds. In a related study, Levy and Szwarc developed a method for determining the reactivities of methyl radicals toward a series of aromatic hydrocarbons.⁷ The similarity of the results implies that

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radicals add to that particular carbon atom in the systems having the largest F_{\max} .⁷

The above results were substantiated further in a more recent theoretical study.⁸ Dewar and Thompson have shown that an excellent linear relationship exists between the logarithms of the relative rates of methyl radical addition⁷ and localization energies for free-radical substitution (*i.e.*, the π -energy differences of the σ complexes and the parent arenes, calculated by a SCF-LCAO-MO approach). So while it is noted that the relative rate data can be correlated with free valence,^{6,7} the perhaps more significant correlation with radical localization energies⁸ also exists. The correlation with localization energy has been advocated as providing the best theoretical measure of the reactivity of a position toward free radicals.⁹ In correlating the rates of radical formation with such differences in energies, the Hammond postulate¹⁰ suggests that the transition states should resemble the σ complexes.

The problem which was faced in our prior work on the arylmethanes concerned the evaluation of the extent of this competing ring reaction with the hydrogen abstraction process. From the data available in the literature on the effects of substituents in the reaction of anthracene derivatives with the trichloromethyl^{11,12} and cyanoisopropyl^{12,13} radicals, we were led to believe that substituents had only small effects on the substitution reaction and that the reactivities did not vary in a regular sense with the electronic character of the substituent. From this information we had made the assumption that 9-methylanthracene and anthracene itself would show approximately the same tendency to undergo ring reaction.^{3,4} Competitive reactions between anthracene and 9-methylanthracene were, therefore, utilized to determine the extent of hydrogen abstraction in the latter system. The same technique was extended to determine the extent of hydrogen abstraction in the other arylmethanes as well. Despite the fact that we did not question this approach when our original work was submitted, we became troubled by the possibility that substituent groups could play a distinct role in determining the course of further radical substitution. It also became increasingly difficult to believe, despite the results of some MO calculations, that any substituent, regardless of its electronic nature, should favor ring reaction.¹⁴ It had been reasoned by Greenwood that the free valence at atom 10 of the anthracene nucleus increases in passing from the parent hydrocarbon to any 9-substituted derivative and should be paralleled by an increase in reactivity at that position. Despite the supportive results of Farenhorst and Kooyman,^{12,13} however, we felt the electronic nature of the substituent would be an important factor in determining rates of reaction.

We now report on a study undertaken to examine the effects of substituents in the radical trichloromethyl-

tion of 9-substituted anthracenes. This series of compounds was chosen for a variety of reasons. Anthracene derivatives should be appreciably more susceptible to substituent effects than other, common polynuclear aromatic systems.¹⁵ With respect to the possible sites of radical attack, the relatively high reactivity of the meso positions should increase the selectivity of the overall process. Also, anthracene should undergo reaction toward trichloromethyl radical at rates about 10^5 that of benzene, 3×10^3 that of chrysene, and approximately 3×10^2 that of pyrene with respect to the most active sites in each molecule.⁶ Unless abstractable hydrogen atoms are present, the anthracene derivative should react mostly in the meso positions. Based upon kinetic results and the argument that a substituent should exercise a retarding steric effect, Kooyman predicted that 9-substituted anthracenes should preferentially react in the 10 position.¹¹⁻¹³ A recent CIDNP investigation of the addition of the cyanoisopropyl radical to 9-bromoanthracene shows this to definitely be the case.¹⁶ Also, since it is generally acknowledged that polar effects accompany the reactions of trichloromethyl radical, we wished to see if a regular variation of reactivity with the electronic character of the substituent would evolve. Finally, it was hoped to determine whether any serious error had been introduced into our work on the arylmethanes by the approach then utilized.

Results and Discussion

The radical addition reactions of trichloromethyl toward the series of 9-substituted anthracenes were run in replicate relative to *trans*-stilbene. Reactions were carried out in sealed ampoules under a reduced pressure of nitrogen at $70.0 \pm 0.2^\circ$. The solvent was a benzene-bromotrichloromethane mixture. Benzene and bromotrichloromethane were maintained at a constant mole to mole ratio of 3:2 and the mole fraction of each was constant throughout all kinetic runs. Possible changes in complexation factors of the trichloromethyl radical with solvent¹⁷ affecting the rates were thereby avoided. The radical initiator was benzoyl peroxide. Solubility problems made direct competition between two anthracene derivatives prohibitive; this was overcome by having an anthracene derivative and *trans*-stilbene compete directly for the trichloromethyl radical. The addition of bromotrichloromethane to the intercycle double bond of stilbenes is known to proceed smoothly.¹⁸ The relative rates of disappearance of substituted anthracenes to *trans*-stilbene were determined *via* gas-liquid chromatography. Full details for the kinetic determinations are outlined in the Experimental Section. The rate data were expressed relative to the parent hydrocarbon, anthracene, and are shown in Table I.

As can be seen from the results presented in Table I, the rates of reaction of anthracenes toward trichloromethyl radical are affected by the nature of the substituent. Anthracenes with electron-donating substituents show enhanced rates and those with electron-withdrawing

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Table I. Relative Reactivities of 9-Substituted Anthracenes toward Trichloromethyl Radical Addition at 70.0°^a

Substituent	k_X/k_H	No. of kinetic runs
NO ₂	0.71 ± 0.10 ^b	7
CN	0.34 ± 0.04	5
CO ₂ CH ₃	0.74 ± 0.07	5
Br	1.00 ± 0.04	7
Cl	1.02 ± 0.04	7
H	1.00	7
C ₆ H ₅	2.28 ± 0.43	7
<i>i</i> -C ₃ H ₇	2.38 ± 0.30	6
C ₂ H ₅	3.39 ± 0.44	10
CH ₃	6.85 ± 0.89	6
OCH ₃	5.52 ± 0.60	5

^a All results obtained relative to stilbene. ^b Average deviation.

substituents show retarded rates relative to the parent hydrocarbon. Figure 1 shows a graphical representation of these results presented in the form of a linear free energy relationship. The logarithms of the relative rates of reaction are plotted against the σ_p^+ parameters of Brown and Okamoto.¹⁹ The same function is almost universally encountered in correlations of the formation of benzylic type radicals. It would seem logical to expect these parameters to be operative in all cases, such as the present study, where direct resonance interaction between the substituent and the site of radical formation can occur. Utilizing 9 of the 11 points (excluding nitro and methyl), a linear relationship is obtained with a slope (ρ^+) of -0.83 and a good correlation coefficient of 0.970. The ρ^+ value appears quite reasonable and comparable in magnitude to that found for hydrogen abstractions from substituted allylbenzenes (-0.64),²⁰ a system where resonance stabilization of the resultant radicals by substituents is not unlike that in the present situation.

We feel that the deviation of the methyl and nitro points are of considerable interest. The methyl compound exhibits the highest reactivity of all compounds in the series. This is the result of loss of this material *via* hydrogen abstraction from the exocyclic methyl position as well as ring substitution. The present correlation estimates the relative amounts of side-chain reaction and ring reaction to be 65 and 35%, respectively. The originally chosen values in our previous report on the arylmethanes were 83 and 17%.^{3,4} In that study the logarithms of the relative rates of hydrogen abstraction from the arylmethanes were plotted against the change in π -binding energy between the arylmethyl radicals and the parent arenes as calculated by a SCF-LCAO-MO approach. This yielded a line with slope $+5.45$ and correlation coefficient of 0.977. With our present correction for the 9-methylanthracene point incorporated into that work the slope of the line is changed to $+5.34$ with a correlation coefficient of 0.973. With this, it is seen that the overall change introduced into the linear free energy relationship of hydrogen abstraction from arylmethanes is approximately 2%. This result satisfied our curiosity into what we felt may have been the largest source of error which was incorporated into our previous work and shows that those results are not significantly affected.

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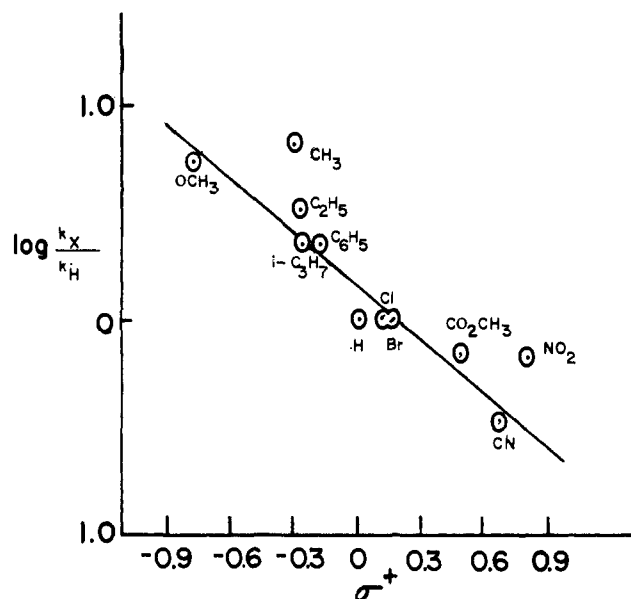
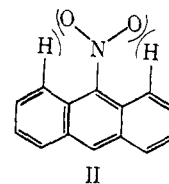


Figure 1. Correlation of $\log k_X/k_H$ and σ_p^+ for the radical trichloromethylation of 9-substituted anthracenes.

It is felt that the upward deviation of 9-nitroanthracene from the correlation line is a result of steric inhibition of resonance. The nitro group is necessarily treated as an electron-withdrawing substituent by virtue of both inductive and resonance criteria. The latter, however, demands coplanarity of the aryl and nitro moieties. While it has been shown that nitrobenzene is planar in the crystal,²¹ complete coplanarity is absent in the *p*-dinitrobenzene system.²² In this compound the angle of inclination of the nitro groups toward the benzene ring is 9.5°. This should still, however, allow for extensive delocalization. Such should not be the case for 9-nitroanthracene. Nonbonded interactions between the nitro group and the hydrogen atoms at positions 1 and 8 (see structure II) should



definitely preclude coplanarity. An X-ray structure determination on 9-nitroanthracene by Trotter has shown that in the solid phase the nitro group is nearly perpendicular (85°) to the aromatic system.²³ Trotter has subsequently argued that a less severe deviation from planarity might exist in solution,²⁴ although one must still conclude that much of the electron-withdrawing tendencies of the nitro group are not present in this molecule. With the effect of the nitro group diminished in this way, 9-nitroanthracene exhibits a much larger relative rate than would be expected otherwise.

It is interesting to note that substituents in other 9-substituted anthracenes also deviate appreciably from planarity. Both carbomethoxy and methoxy are far

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(23) J. Trotter, *Acta Crystallogr.*, **12**, 237 (1959).

(24) J. Trotter, *Can. J. Chem.*, **37**, 1009 (1959).

from coplanar with the anthracene system, the deviations being 73 and 86°, respectively.²⁵ Carbomethoxy should qualitatively resemble nitro in its electronic properties and it does show a slight upward deviation from the correlation line. While this may be due to some steric inhibition of resonance, the departure from the correlation is approximately within the experimental uncertainty. We have, therefore, chosen to treat the results for 9-carbomethoxyanthracene as representing a "normal" effect. The electronic properties of the methoxy group differ greatly from the others just discussed in possessing a resonance effect which is electron donating. Though nonplanarity should theoretically remove this effect, the kinetic results show no departure from expectation. The nonplanar structure does not preclude potential resonance stabilization, however. The π system of electrons of the aromatic ring can now interact with the lone pair of electrons in the oxygen sp^2 orbital. This interaction should be substantial and, we feel, is the reason for the expected behavior of the methoxy compound. The phenyl group in 9-phenylanthracene is also most likely out of the plane of the anthracene system. Here again, electron release should not be as effective as if the phenyl group was coplanar. However, the good correlation obtained is not unexpected since the reaction series used to develop the σ_p^+ values¹⁹ most probably had the phenyl substituent in a noncoplanar arrangement also. Indeed, a recent report in the literature shows that a new σ_p^+ value has been developed for phenyl in a known coplanar arrangement.²⁶ The greater negative value assigned to σ_p^+ for phenyl in that situation indicates that a planar phenyl group is more electron releasing than a methyl, a situation which does not exist in the present study.

Finally, we should comment upon the reactivities of the two other 9-alkylanthracenes in addition to those comments already offered about 9-methylanthracene. As stated, 9-methylanthracene undergoes a considerable amount of hydrogen abstraction from the exocyclic methyl accounting for a large portion of its reactivity. The formation of the benzylic type radical in this process necessarily leads to a situation where peri interactions between the exocyclic hydrogen atoms and the hydrogen atoms in positions 1 and 8 may come into play. This type of interaction may cause lessened stabilization of the radical intermediate due to a loss of coplanarity of the exocyclic position with respect to the anthracene system. It has been shown, however, that these unfavorable interactions in the 1-methylnaphthalene case may be lessened by in-plane bending deformations at both the exocyclic carbon and the carbon to which it is attached along with an out-of-plane deformation of one hydrogen at the exocyclic site and an opposite such deformation at the peri position.²⁷ A somewhat analogous situation may exist in the case of 9-methylanthracene, allowing significant hydrogen abstraction even though two peri hydrogen atoms have to be reckoned with. Increasing α substitution yielding the cases of 9-ethyl- and 9-isopropylanthracene makes much more significant the problem of peri interactions and the very large probability that these two com-

pounds undergo hydrogen abstraction to only a very small extent. This is, in essence, substantiated by including these compounds in the overall correlation and noting only very small deviations from the relation obtained. Indeed, preliminary strain energy calculations show that a planar radical intermediate resulting in hydrogen abstraction from 9-isopropylanthracene has a prohibitively large nonbonded interaction strain term, while the more strain-free perpendicular structure allows for no radical delocalization into the anthracene nucleus. Figure 1 shows that the reactivity of the 9-isopropylanthracene is essentially that of a compound undergoing only the radical addition process. The point for 9-ethylanthracene is slightly more off the correlation line; this may be an indication that a small amount of this compound is reacting *via* the hydrogen abstraction process. These results are qualitatively in accord with a study reported on the free-radical halogenation of 9-alkyl- and 9-arylanthracenes with iodobenzene dichloride which yielded similar relative rate data for the three alkylanthracenes we have included in this study.²⁸ In that case also, the methyl compound was much more reactive than the other two alkyl systems.

In conclusion, we feel that the significance of this work lies essentially in the fact that we have conclusively shown that little error was introduced into our work on the arylmethanes by the assumptions then made. In that process we have observed another instance where the reaction of trichloromethyl is influenced by electronic effects as evidenced in the good correlation with the σ_p^+ substituent parameters. That this correlation was observed in a polynuclear aromatic system is also deemed of great interest.

Experimental Section

Melting points were taken in unsealed capillary tubes with a Mel-Temp melting point apparatus and are uncorrected. Gas-liquid chromatography analyses were carried out with a Varian Aerograph 202-B gas chromatograph equipped with a linear temperature programmer and a Hewlett-Packard 3373B digital integrator. The column utilized in this investigation was a 12 ft \times 0.25 in. aluminum column of 5% SE-30 on Chromosorb W.

Materials. Bromotrichloromethane and benzene were purified by standard techniques. Benzoyl peroxide (Matheson Coleman and Bell), *p*-dibromobenzene (Matheson Coleman and Bell), and *trans*-stilbene (Matheson Coleman and Bell, Scintillation Grade) were used with no further purification. Anthracene, 9-bromoanthracene, and 9-methylanthracene (Aldrich) were used as commercially obtained.

9-Chloroanthracene was prepared *via* the reaction of anthracene with anhydrous cupric chloride in refluxing CCl_4 ,²⁹ mp 98–100° (lit.²⁹ mp 104–106°).

9-Cyanoanthracene was prepared from 9-anthraldehyde by conversion to its oxime and subsequent dehydration with acetic anhydride,³⁰ mp 177–178° (lit.³⁰ mp 177.5–179°).

9-Methoxyanthracene was obtained from the reaction of anthrone and aqueous sodium hydroxide followed by addition of methyl *p*-toluenesulfonate,³¹ mp 94–96° (lit.³¹ mp 95–96°).

Methyl 9-anthroate was prepared from the reaction of 9-anthropic acid with methanol in benzene and trifluoroacetic anhydride according to the method of Parish and Stock,³² mp 111–112° (lit.³³ mp 112.7–113.2°).

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9-Nitroanthracene was obtained *via* the direct nitration of anthracene,³⁴ mp 142–144° (lit.³⁴ mp 145–146°).

9-Ethylanthracene, 9-isopropylanthracene, and 9-phenylanthracene were prepared from the reaction of anthrone with the appropriate Grignard reagent,³⁵ the product of which underwent spontaneous dehydration to yield the desired 9-substituted anthracenes: 9-ethylanthracene, mp 54.5–56.5° (lit.³⁶ mp 59°); 9-isopropylanthracene, mp 76–77° (lit.³⁶ mp 75–76°); 9-phenylanthracene, mp 148.5–151.5° (lit.³⁷ mp 152–153°).

All of the materials used in this investigation had purities in excess of 98% as determined by glpc.

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Procedure for Kinetic Studies. A solution of the substituted anthracene, *trans*-stilbene, *p*-dibromobenzene, bromotrichloromethane, and benzene was prepared in the approximate molar ratio of 1:2:1:50:75. A small amount was reserved for analysis as starting material. The remainder was divided among ampoules containing a small amount of benzoyl peroxide. The ampoules were sealed under a reduced pressure of nitrogen and then placed in a constant-temperature bath at $70.0 \pm 0.2^\circ$ for 77–122 hr during which time 14–73% of the substituted anthracene had been consumed. After completion of the reaction, the ampoules were cooled and opened and analyzed for the disappearance of substituted anthracene and *trans*-stilbene *via* glpc using *p*-dibromobenzene as an internal standard. The relative rates of reaction, $k_{\text{substituted anthracene}}/k_{\text{trans-stilbene}}$, were then determined by standard techniques.³⁸

Acknowledgment. We thank Oregon State University Computer Center for supplying the necessary funds for the calculations.

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Charge-Transfer Spectra of Some Phenyl and Naphthyl Derivatives. Relative Importance of σ - π and n - π Conjugation Involving the π Si-Si System¹

Hideki Sakurai* and Mitsuo Kira

Contribution from the Department of Chemistry, Faculty of Science, Tohoku University, Aobayama, Sendai, Japan. Received May 29, 1973

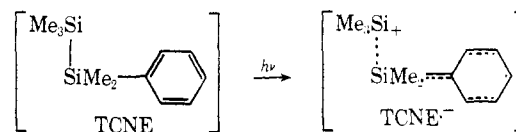
Abstract: The ionization potentials of several α -naphthyl, β -naphthyl, and phenyl derivatives (Ar-X, X = Me₃Si-SiMe₂, Me₃SiCH₂, MeO, and CH₃) have been determined by charge-transfer spectra. These data were used to evaluate the relative efficiencies of σ (or n)- π conjugations by using the first-order perturbation theory. It is shown that a silicon 3p orbital is only one-third as effective as carbon or oxygen 2p orbital to overlap with carbon π systems. The considerable σ - π interaction seen in Si-Si π systems may be attributed to the very high energy of the Si-Si σ orbital.

It has been reported in 1964 that the silicon-silicon bond has conjugating properties with phenyl and vinyl groups.²⁻⁴ These "conjugating properties" have been rationalized at first in terms of "d- π " interaction in the excited state.²⁻⁷ Later, the ground-state interaction between the silicon-silicon σ bond and the π system was recognized as an important factor in addition to d- π^* interactions.

Although inductive polarization of benzene molecular orbitals by the β -trimethylsilyl group has been suggested,⁸ the importance of σ - π conjugation between the Si-Si bond and the benzenoid π system has been indicated recently by reaction,⁹ electronic and charge-

transfer (CT) spectra,^{10,11} stereoelectronic aspects,¹² and photoelectron spectroscopy.¹³

The importance of such a σ - π conjugation has been recognized in general by Traylor and coworkers¹⁴ in a number of chemical and spectroscopic investigations. In terms of σ - π conjugation, the vertical stabilization by the silicon-silicon bond in the charge-transfer complex must involve a silicon-carbon double bond.



In spite of the increasing evidence for the silicon-

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