

# Halogen Abstraction Studies. V. Abstraction of Iodine by Phenyl Radicals from Iodonaphthalenes, Iodopyridines, and Iodothiophenes. The Question of Polar Effects<sup>1,2</sup>

Wayne C. Danen,\* Donald G. Saunders,<sup>3</sup> and Kenneth A. Rose

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506. Received August 13, 1973

**Abstract:** The rate of abstraction of iodine by phenyl free radicals from the isomeric iodonaphthalenes, iodopyridines, and iodothiophenes relative to the rate of abstraction of chlorine from carbon tetrachloride is reported. The rates obtained can be correlated with the  $\pi$ -electron density at the carbon to which the iodine is attached as calculated by simple HMO theory. Qualitatively, excess electron density at the carbon retards abstraction and deficient electron density enhances the rate. These results parallel earlier studies of substituent effects on the rate of halogen abstraction from both aromatic and aliphatic halides in which electron-withdrawing substituents were noted to enhance the rate of homolytic halogen removal while electron-donating groups retarded abstraction. 2-Iodopyridine is the fastest reacting compound in the present study with  $k_1/k_{Cl} = 106$ ; 3-iodothiophene is slowest with a value of 4.0. The relative rates show no correlation with C-Br bond dissociation energies for the corresponding aryl bromides. This fact and the dependence of the rates upon electron densities is interpreted in terms of a polar effect which overrides the differences in bond dissociation energies.

The abstraction of a univalent atom is probably the most common mode of reaction of a free radical and a voluminous amount of research dealing with hydrogen abstraction reactions has been reported.<sup>4-7</sup> Other than hydrogen, the halogens are the only univalent substituents normally found in organic molecules and we have in the last several years conducted investigations on the factors influencing the rates of abstraction of halogen atoms from several types of organic bromides and iodides.<sup>2,8-10</sup> In particular, we have elucidated a unique polar effect operative in the homolytic abstraction of a halogen atom,<sup>8,9</sup> determined the occurrence of neighboring halogen participation in such processes,<sup>9</sup> provided an assessment of the relative stabilities of various bridgehead radicals,<sup>10</sup> and investigated electronic-steric effects in ortho-substituted iodobenzenes.<sup>2</sup>

Although the free-radical abstractions of hydrogen and halogen atoms have some features in common, the latter surpasses hydrogen abstraction in many respects as a means of generating free radicals for the study of homolytic processes in organic compounds. First of all, the abstraction of a halogen atom produces a free radical at a specific site within a molecule. The site may be specified exactly by the choice of the appropriate organic halide which can normally be synthesized without difficulty. There is usually a multitude of different types of C-H bonds within even a relatively simple

organic molecule and many competitive hydrogen abstractions result. Secondly, a choice of halogens is available from which to choose offering an investigator a wide range of reactivities, one of which should prove suitable for his system and measuring technique. Such a choice is not available with hydrogen, of course (replacement by deuterium or tritium offers but a slight kinetic difference). Thirdly, the relatively high reactivity of certain halogen substituents, particularly bromine and iodine, allows one to investigate abstraction processes in systems completely inaccessible *via* hydrogen atom abstraction. The last feature is pertinent to the present study in which we report the relative rates of abstraction of iodine from the isomeric iodonaphthalenes, iodopyridines, and iodothiophenes. The direct abstraction of an aromatic hydrogen is not feasible under these conditions, of course.

## Results

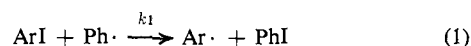
The relative rates listed in Table I were obtained by

**Table I.** Rates of Iodine Abstraction by the Phenyl Radical at 60° vs. the Rate of Abstraction of Chlorine from Carbon Tetrachloride

Organic halide	$k_1/k_{Cl}$	$q^a$	$D(Ar-Br)^b$
1-Iodonaphthalene	22.0	0.9933	70.9
2-Iodonaphthalene	17.4	0.9946	70.0
2-Iodopyridine	106	0.9015	71.5
3-Iodopyridine	25.6	0.9995	75.9
4-Iodopyridine	31.2	0.9276	
Iodobenzene	16-18 <sup>c</sup>	0.9949	70.9
2-Iodothiophene	4.6	1.1598	68.5
3-Iodothiophene	4.0	1.1466	

<sup>a</sup>  $\pi$ -Electron density at carbon to which iodine is attached as calculated by simple HMO theory. <sup>b</sup> Carbon-bromine bond dissociation energy of corresponding bromide.<sup>16</sup> <sup>c</sup> Estimated from the data in ref 8.

the competitive technique employed in our earlier studies (eq 1 and 2).<sup>9,10</sup> The phenyl radicals were



(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

(2) Part IV: W. C. Danen, D. G. Saunders, and K. A. Rose, *J. Amer. Chem. Soc.*, **95**, 1612 (1973).

(3) National Science Foundation Undergraduate Research Participant, summer, 1968.

(4) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, pp 149-177.

(5) R. S. Davidson, *Quart. Rev., Chem. Soc.*, **21**, 249 (1967).

(6) A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, **1**, 1 (1965).

(7) J. M. Tedder, *Quart. Rev., Chem. Soc.*, **14**, 336 (1960).

(8) W. C. Danen and D. G. Saunders, *J. Amer. Chem. Soc.*, **91**, 5924 (1969).

(9) W. C. Danen and R. L. Winter, *J. Amer. Chem. Soc.*, **93**, 716 (1971).

(10) W. C. Danen, T. J. Tipton, and D. G. Saunders, *J. Amer. Chem. Soc.*, **93**, 5186 (1971).

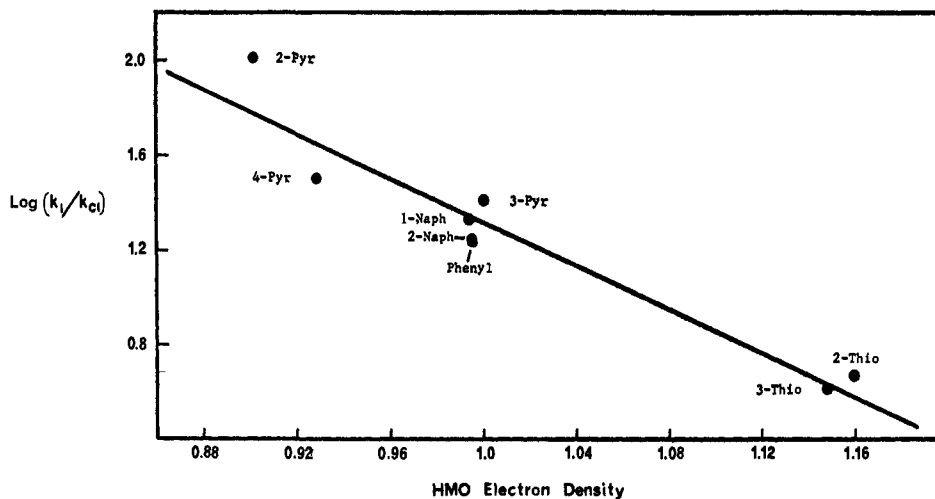
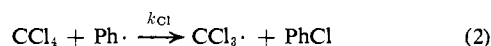


Figure 1. Correlation of  $\log(k_I/k_{Cl})$  values for the isomeric iodonaphthalenes, iodopyridines, iodothiophenes, and iodobenzene with the Hückel  $\pi$ -electron density on the carbon to which the iodine is attached (correlation coefficient = 0.955).



generated by decomposition of phenylazotriphenylmethane at  $60.0 \pm 0.1^\circ$  and the relative reactivity of the iodo compound per molecule of carbon tetrachloride

$$k_I/k_{Cl} = [\text{C}_6\text{H}_5\text{I}][\text{CCl}_4]/[\text{C}_6\text{H}_5\text{Cl}][\text{ArI}] \quad (3)$$

was calculated from eq 3; estimated reliability is  $\pm 5\%$ .

Also included in Table I is the  $\pi$ -electron density  $q$  at the carbon to which iodine is attached in the various aromatic iodides. These electron densities were calculated by simple Hückel molecular orbital theory utilizing the following parameters:  $h_C = 0.0$ ,  $k_{C-C} = 1.0$ ;  $h_N = 0.50$ ,  $k_{C-N} = 0.8$ ;  $h_S = 0.0$ ,  $k_{C-S} = 0.6$ ;  $h_I = 1.25$ ,  $k_{C-I} = 0.25$ . These values are those suggested by Streitwieser<sup>11</sup> for carbon and nitrogen; values for iodine were not available but were assigned as being reasonable and consistent with related heteroatoms. The parameters for sulfur were those suggested by Pilar and Morris.<sup>12</sup>

## Discussion

From the data in Table I it is observed that, with the exception of 2-iodopyridine and the iodothiophenes, the rates of abstraction of iodine from the iodonaphthalenes and iodopyridines are not *drastically* different from that for iodobenzene. This is as expected since the homolytic removal of an iodine atom attached to any of these aromatic systems results in the formation of a  $\sigma$  free radical with the unpaired electron in a more or less  $sp^2$  hybridized orbital. This orbital lies in the nodal plane of the carbon  $p$  orbitals so the extent of conjugation in the  $\pi$  system, heteroatoms in the aromatic ring, and other perturbations on the  $\pi$  electrons cannot interact directly with the unpaired electron (except possibly for the 2-pyridyl and 2-thiophyl radicals).

In spite of the fact that a  $\sigma$  radical is undoubtedly

being formed in all cases, there are distinct differences in the reactivities of certain of the aromatic iodides reported in Table I. The iodopyridines, in particular 2-iodopyridine, are all more reactive than iodobenzene while the two iodothiophenes are both less reactive; the iodonaphthalenes resemble iodobenzene most closely. These observations suggest that the relative electron densities on the various carbon atoms in these aromatic compounds are influencing the rates of removal of the iodine atoms. Moreover, the effects are exactly those we would predict on the basis of our earlier studies of substituent effects on the free-radical abstraction of halogen atoms, namely, that an increase in electron density retards abstraction and a withdrawal of electron density enhances the homolytic removal of the halogen atom.<sup>2,8,9</sup> In the present case, the electronegative nitrogen atom in pyridine removes electron density from the remaining atoms of the ring enhancing the rate of abstraction of iodine while the pair of electrons donated by the sulfur atom in thiophene effectively increases electron density on the carbon atoms of the ring resulting in a slower rate of iodine removal.

The generalizations of the preceding paragraph can be placed on a somewhat more quantitative basis by comparing the relative rates of abstraction of iodine with the HMO calculated  $\pi$ -electron densities on the carbons to which the iodines are attached. The calculated electron densities are listed in Table I; Figure 1 is a graphic correlation between  $\log k_I/k_{Cl}$  and the calculated  $\pi$ -electron densities. Although the correlation can hardly be considered excellent, there is a correspondence between the calculated electron densities and the rates.<sup>13</sup>

The present results contrast studies of homolytic iodine exchange in similar compounds which proceed *via* an addition-elimination complex mechanism in which the two iodines are attached symmetrically to the same carbon.<sup>14</sup> The rates of iodine exchange in 1- and 2-iodonaphthalene, several substituted iodobenzenes,

(11) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 135.

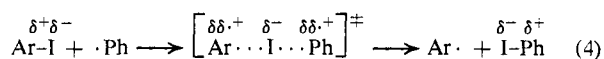
(12) F. L. Pilar and J. R. Morris, *J. Chem. Phys.*, **34**, 389 (1961). There do not appear to be any generally accepted HMO parameters for the sulfur atom in thiophene. The parameters utilized may overestimate the electron density at the carbon atoms in thiophene as evidenced by comparison of the results of Pilar and Morris with the more rigorous, albeit still semiempirical, CNDO method: D. T. Clark, *Tetrahedron*, **24**, 2663 (1968).

(13) At the suggestion of a referee, an attempt was made to correlate the  $\log k_I/k_{Cl}$  values with atom-atom self-polarizabilities for the carbon atoms of the C-I bonds in the reactants. No significant correlation was noted possibly because of the small degree of ionic character developed in these homolytic reactions.

(14) M. Nakashima, C. Y. Mok, and R. M. Noyes, *J. Amer. Chem. Soc.*, **91**, 7635 (1969).

and the 1,2-diiodoethylenes do not correlate with electron densities but instead with HMO calculated localization energies. Such calculations provide an estimate of the resonance energy lost when an  $sp^2$  carbon of the original aromatic system is converted into a nonconjugative  $sp^3$  carbon.

The correlation between the rate of iodine abstraction and the calculated electron densities can be accounted for in terms of a polar effect as has been observed in our previous studies.<sup>2,8,9</sup> However, it does not appear possible to unambiguously distinguish whether the substituents operate predominantly in the transition state as is usually argued or whether the influence is on the ground states of the aromatic iodides. The key point is that the carbon atom to which iodine is bonded in the original aryl iodide is presumably somewhat electron deficient at the onset of homolytic iodine removal because of the polarized C–I bond resulting from the inductive effect of the electronegative iodine<sup>15</sup> and that *this carbon atom acquires an increased amount of electron density in the transition state relative to the ground state* (eq 4). There is a net transfer of electron density from



the attacking phenyl radical to the newly forming aryl radical. It is possible that perturbations which increase the electron density at this carbon stabilize the ground state and perturbations which decrease the electron density destabilize the ground state while neither type strongly perturbs the transition state. Accurate bond dissociation energies, unfortunately, are not available for these compounds. However, bond dissociation energies<sup>16</sup> for the C–Br bond of the corresponding aryl bromides are available and are given in Table I. The values for  $D(\text{Ar-Br})$  were all obtained by the same research group from pyrolyses utilizing the toluene carrier gas technique and were considered reliable within 1.5–2.0 kcal/mol;<sup>16</sup> they hopefully are reasonably accurate at least in a relative order. If it is assumed that the  $D(\text{Ar-Br})$  values for the bromo compounds are proportional in some manner to  $D(\text{Ar-I})$  values, several interesting observations can be made. First of all, the  $D(\text{Ar-Br})$  values for bromobenzene, 1-bromonaphthalene, and 2-bromonaphthalene are very similar as are the corresponding  $k_I/k_{Cl}$  values for these compounds. The largest bond energy is for 3-bromopyridine while the  $k_I/k_{Cl}$  value for the corresponding iodide would suggest that  $D(\text{Ar-Br})$  should be quite similar to bromobenzene or the bromonaphthalenes. The fastest reacting compound, 2-iodopyridine, has  $D(\text{Ar-Br}) = 71.5$  kcal/mol which suggests it should react somewhat slower than iodobenzene or the iodonaphthalenes. Surprisingly 2-iodothiophene has the lowest  $D(\text{Ar-Br})$  value, 68.5 kcal/mol, which is just the opposite of that anticipated from the rate data. The large difference in bond energy between 2- and 3-bromopyridine is reflected in the corresponding  $k_I/k_{Cl}$  values; however, the  $D(\text{Ar-Br})$  values for both pyridines are significantly greater than the value for bromobenzenes even though these

compounds are appreciably more reactive to halogen abstraction than bromobenzene.

Szwarc and coworkers have also determined C–Br bond dissociation energies for a variety of monosubstituted bromobenzenes<sup>16</sup> for which we have determined  $k_I/k_{Cl}$  values for the corresponding iodides.<sup>2,8</sup> We have shown in this work that the  $k_I/k_{Cl}$  values can be correlated with the calculated electron densities for the carbon atoms originally bearing the iodine atom; our previous studies have shown that there is a distinct relationship between the  $k_I/k_{Cl}$  values for monosubstituted iodobenzenes and Hammett substituent constants which also are a measure of the electron density at a reaction site. Since both the BDE and  $k_I/k_{Cl}$  values reflect the homolytic cleavage of a C–Br bond, the total lack of any correlation between these functions (*cf.* Figure 2) indicates that the attacking free radical in the abstraction process has a decisive influence on the rates of the reactions, *i.e.*, the  $k_I/k_{Cl}$  values. It appears that the function of the attacking radical is to supply electron density in the transition state to the region of the original C–I bond (*cf.* eq 4). Such an interaction constitutes a polar effect for these homolytic halogen abstractions even though the carbon atom to which the iodine is originally bonded might well become less charged in the transition state.

Zavitsas has recently challenged the importance and, indeed, the need for the concept of the polar effect in homolytic hydrogen abstraction reactions.<sup>17</sup> Instead of charge separation in the transition state this author attributes variations in energies of activation for the abstraction of a hydrogen atom primarily to differences in C–H bond dissociation energies and vibrational stretching frequencies of the reacting moieties. Zavitsas' postulates appear, however, to have failed a crucial test insofar as a  $\rho$  value of  $-1.4$  is predicted for reaction of the *tert*-butyl radical with substituted toluenes; Pryor and coworkers have obtained an experimental  $\rho$  value of  $+0.99 \pm 0.04$  in agreement with polar effect considerations.<sup>18</sup>

There is no question, however, that the strength of the bond being broken in a homolytic reaction is an important factor in the kinetics of the reaction.<sup>5-7,19</sup> Indeed, we have shown in previous studies that the rate of abstraction of iodine from a variety of aliphatic iodides in which polar effect differences were minimized could be correlated very well with the respective bond dissociation energies.<sup>10</sup> The absence of correspondence between  $\log(k_I/k_{Cl})$  values in the present study and the respective Ar–Br bond dissociation energies (Figure 2) and the apparent relationship of the kinetic values to the electron density at the carbon to which the halogen is attached (Figure 1 and ref 2, 8–10) suggest that polar effects *override* the relatively small differences in bond dissociation energies in these systems.

In our previous study of abstraction of iodine from aliphatic iodides,<sup>10</sup> the  $k_I/k_{Br}$  relative reactivities ranged from 0.17 (methyl iodide) to 1.09 (*tert*-butyl iodide) which corresponds to  $\Delta\Delta G^\ddagger$  of 1.2 kcal/mol at 60°. The corresponding  $\Delta\text{BDE}$  amounted to 6.3 kcal/mol

(15) It may be noted that both carbon and iodine have the same electronegativity (2.5) on the Pauling scale. However, this value for an isolated carbon atom may not be realistic for a highly substituted carbon atom as is found in an organic molecule.

(16) (a) M. Ladacki and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **219**, 341 (1953); (b) M. Szwarc and D. Williams, *ibid.*, **219**, 353 (1953).

(17) (a) A. A. Zavitsas and J. A. Pinto, *J. Amer. Chem. Soc.*, **94**, 7390 (1972); (b) A. A. Zavitsas, *ibid.*, **94**, 2779 (1972).

(18) W. A. Pryor, W. H. Davis, Jr., and J. P. Stanley, *J. Amer. Chem. Soc.*, **95**, 4754 (1973).

(19) Reference 4, p 154.

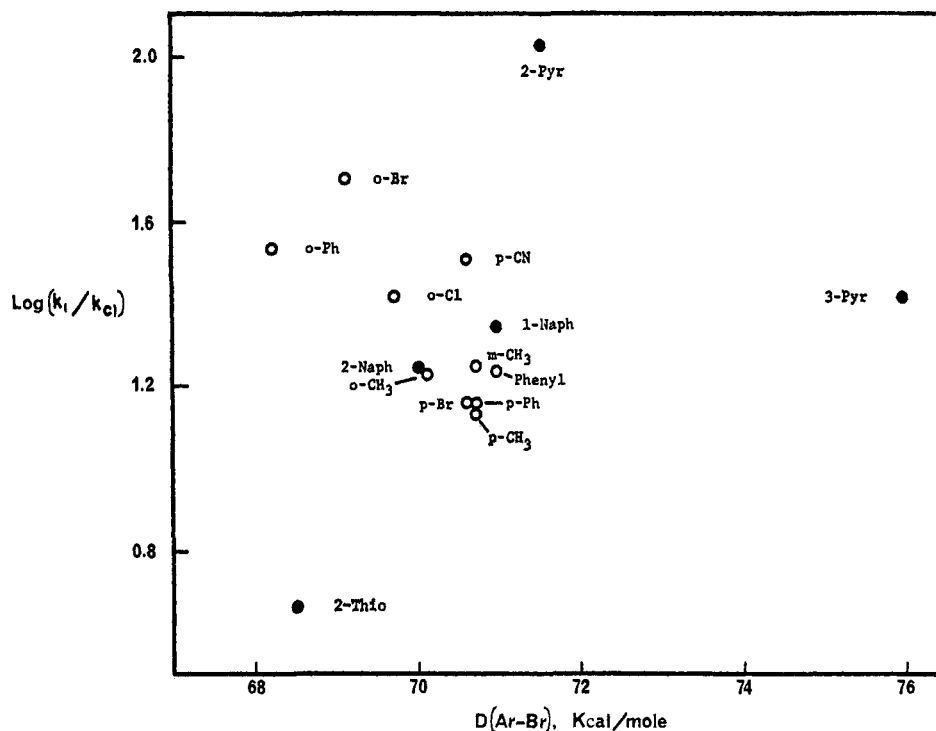


Figure 2. Attempted correlation of  $\log(k_1/k_{c1})$  values for various aryl iodides with the bond dissociation energies of the corresponding aryl bromides: (●) compounds determined in the present study; (○) substituted iodobenzenes.

(56.3 and 50 kcal/mol for methyl iodide and *tert*-butyl iodide, respectively). In the present study the spread of reactivities for which BDE values are available covers from 4.6 (2-iodothiophene) to 106 (2-iodopyridine) which yields a  $\Delta\Delta G^\ddagger$  of 2.1 kcal/mol at 60°, while the corresponding  $\Delta$ BDE for the aryl bromides is  $-3.0$  kcal/mol (minus sign because the change is in the opposite sense; the more reactive 2-iodopyridine actually has a higher BDE; and the  $\Delta$ BDE for the aryl iodides is expected to be more compressed). In the latter case it is obvious that something is affecting the rate of iodine abstraction but that this influence is not related only to the overall  $\Delta H$  of the reaction.

Attempted least-squares correlations between  $\log(k_1/k_{c1})$ , HMO calculated electron densities ( $q$ ), and bond dissociation energies (BDE) yielded the following results (eq 5–7).<sup>20</sup> It is quite apparent that the rates of

$$\log(k_1/k_{c1}) = -4.83q + 0.01(\text{BDE}) \quad (r = 0.953) \quad (5)$$

$$\log(k_1/k_{c1}) = -0.08(\text{BDE}) \quad (r = 0.462) \quad (6)$$

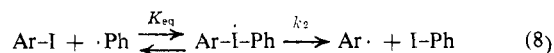
$$\log(k_1/k_{c1}) = -4.96q \quad (r = 0.952) \quad (7)$$

abstraction of iodine in the series of compounds investigated in this work are much more dependent upon the electron densities on the carbons to which iodine is attached (eq 5 and 7) than on the bond dissociation energies (eq 5 and 6). If the BDE data are accurate, it seems plausible to conclude that polar effects are indeed real and operating in these homolytic iodine abstraction reactions. However, it must be emphasized that the bond dissociation energies of the aryl bromides must be accurate at least in a relative order and proportional in some manner to the aryl iodides. Although the latter assumption is probably reasonable, there is some question concerning the reliability of the C–Br BDE

(20) Correlation using only those compounds for which both electron densities and BDE values are known (*cf.* Table I).

data.<sup>16,21</sup> If the data are not accurate, the  $k_1/k_{c1}$  values might merely reflect changes in the Ar–I bond strengths and there would be no need to invoke a polar effect argument. *A priori*, it is reasonable to expect that electron-withdrawing groups might weaken and electron-donating groups strengthen the C–I bonds of the reactant molecules because of the dipolar nature of such bonds.

In addition, a phenylaryliodine intermediate, Ar–I–Ph, must not be formed in these reactions. If so, the  $k_1/k_{c1}$  values might not reflect the true rate of iodine abstraction but instead might be related to an equilibrium constant,  $K_{eq}$ , or a composite  $k_2K_{eq}$  (eq 8). The available data, however, appear to rule out such complications.<sup>22</sup>



Furthermore, an alternative explanation for the effect of substituents and electron density on the rates of halogen abstraction cannot be rigorously excluded at the present time. Szwarc has noted that halogen abstractions are slower than anticipated relative to hydrogen abstractions on the basis of bond dissociation energies. This was interpreted as being due to a repulsion between the attacking radical and the closed shell of the halogen atom in the stretched C–X bond.<sup>23</sup> Such repulsions are negligible for hydrogen abstrac-

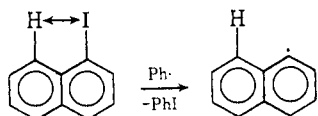
(21) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed, Vol. 1, Reinhold, New York, N. Y., 1954, p 94.

(22) W. C. Danen, *Methods Free-Radical Chem.*, in press.

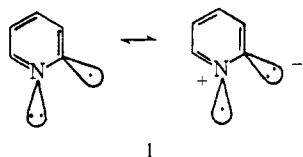
(23) F. W. Evans, R. J. Fox, and M. Szwarc, *J. Amer. Chem. Soc.*, **82**, 6414 (1960); F. J. Fox, F. W. Evans, and M. Szwarc, *Trans. Faraday Soc.*, **57**, 1915 (1961). These workers differentiate between a repulsion effect and a polar effect primarily on the basis of sodium-flame reaction data. More recent workers (K. R. Wilson and D. R. Herschbach, *Nature (London)*, **208**, 182 (1965)) have noted that the electron affinity of the reactant molecule plays a dominant role in this class of reactions and conclude that reactivities are mainly governed by charge delocalization in the transition state, *i.e.*, a polar effect.

tions and should be reduced for halogen abstractions when electron-withdrawing groups are present on the organic halo compound. However, we prefer to interpret the influence of substituents and electron density on the substrate carbon atom on the rate of halogen abstraction as resulting from a polar effect as discussed above since HMO calculations yield a rather invariant  $\pi$ -electron density of  $1.99 \pm 0.01$  on iodine for all the compounds listed in Table I.

From Table I it can be seen that 1-iodonaphthalene is slightly more reactive than either iodobenzene or 2-iodonaphthalene even though all three have approximately identical calculated electron densities on the carbon of the C-I bond. Even though the difference is not large, this might reflect a slight steric acceleration of iodine abstraction resulting in relief of the 1-8 iodine-hydrogen peri interaction although it is expected that such an interaction would also be reflected by a lower C-Br BDE for the 1 isomer.



2-Iodopyridine is the most reactive compound of the present study possibly as a result of a stabilization of the product 2-pyridyl radical *via* interaction with the lone pair of electrons on nitrogen as depicted in 1. Direct evidence for such an interaction in the 2-pyridyl radical has been obtained from electron spin resonance



studies in which a large ( $29 \pm 1$  G) hyperfine interaction

with the nitrogen nucleus was observed.<sup>24</sup> The high reactivity of 2-iodopyridine to phenyl radicals is paralleled by the enhanced reactivity of 2-halopyridines with sodium atoms. Both 2-chloro- and 2-bromopyridine react much more rapidly with sodium atoms than do the corresponding 3-chloro- and 3-bromopyridines. The relative rates are 340:1 and 25:1, for the chlorides and bromides, respectively.<sup>25</sup> Nevertheless, stabilization of the 2-pyridyl radical as depicted in 1 cannot be of an overwhelming nature since the BDE for 2-bromopyridine is higher than that for bromobenzene and the rate of iodine removal is not significantly greater than the rate anticipated on the basis of a polar effect. If there is a strong resonance interaction with the lone pair of electrons on nitrogen, the observed  $k_1/k_{Cl}$  for 2-iodopyridine should be well above the line in Figure 1 while in fact it correlates reasonably well.

### Experimental Section

Iodobenzene, 1-iodonaphthalene, 2-iodonaphthalene, 3-iodopyridine, and 2-iodothiophene were commercially available and purified in all cases by either vacuum distillation or recrystallization. 2-Iodopyridine was prepared from 2-aminopyridine by diazotization followed by reaction with potassium iodide.<sup>26</sup> 3-Iodothiophene was synthesized from the commercially available bromo compound according to the procedure of Gronowitz and Hakansson.<sup>27</sup> 4-Iodopyridine was kindly supplied by Dr. Paul H. Kasai of Union Carbide Corporation.

Kinetic analyses were conducted as described in a previous paper.<sup>9</sup>

**Acknowledgment.** The authors are indebted to Paul H. Kasai of Union Carbide Corporation for kindly supplying a sample of 4-iodopyridine. Helpful discussions with Andreas A. Zavitsas and William A. Pryor are also gratefully acknowledged.

(24) P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **94**, 720 (1972).

(25) E. Warhurst, *Quart. Rev., Chem. Soc.*, **5**, 44 (1951).

(26) J. Halpern and J. P. Maker, *J. Amer. Chem. Soc.*, **87**, 5361 (1965).

(27) S. Gronowitz and R. Hakansson, *Ark. Kemi*, **16**, 309 (1960).

## Unsaturated Carbenes from Primary Vinyl Triflates.

### I. Method and Scope

Peter J. Stang,\* Michael G. Mangum, Dennis P. Fox,<sup>1</sup> and Peter Haak

Contribution from the Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112. Received February 8, 1974

**Abstract:** A variety of primary vinyl triflates, 7-13, containing a hydrogen, dialkyl groups, arylalkyl, or diaryl groups in the  $\beta$  position was prepared from the corresponding aldehydes *via* their silyl enol ethers. Treatment of the dialkyl triflates with *t*-BuOK in a variety of olefins at  $-20$  to  $+25^\circ$  afforded methylenecyclopropanes in good yields together with differing amounts of *tert*-butyl vinyl ethers. Whereas similar treatment of  $\beta$ -aryl and  $\beta$ -hydrogen triflates gave only acetylenes as products. Both the olefin adducts as well as the *tert*-butyl vinyl ethers arise from unsaturated carbenes  $(R)_2C=C:$  or carbenoids. The methods and scope of unsaturated carbene generation from primary vinyl triflates are discussed.

An enormous amount of work has been reported<sup>2</sup> in the area of carbene chemistry since the pioneer-

(1) University of Utah Graduate Research Fellow.

(2) For reviews and leading references, see (a) M. Jones, Jr., and R. A. Moss, "Carbenes," Vol. I, Wiley, New York, N. Y., 1973; (b) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York,

ing investigations of Doering, Hine, Meerwein, and Skell. Besides the simple carbene itself, 1, there is of

N. Y., 1971; (c) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes and Arynes," Appleton-Century-Crofts, New York, N. Y., 1969; (d) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964; (e) D. Bethell, *Advan. Phys. Org. Chem.*, **7**, 153 (1969); (f) R. A. Moss,