communication; R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 7452 (1976).

(11) The PA of toluene corresponds to 189.9 kcal/mol; cf. R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 7452 (1976); W. J. Hehre, R. T. Mc Iver, Jr., J. Pople, and P. v. R. Schleyer, *ibid.*, **96**, 7162 (1974).

(12) The exothermicity of the alkylation process can be approximately evaluated from the ΔH_f^0 value of *p-tert*-butylanisole (estimated from the data taken from D. R. Skull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., (1968), the ΔH_f^0 value of $t\text{-}C_4H_9^+$, from F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970), and assuming that the PA of the ring position of II bearing the alkyl group to be roughly equivalent to that of anisole, 199 kcal/mol. These assumptions lead to a ΔH_f^0 value of ca. 125 kcal/mol for II, and to a ΔH^0 value of ca. −30 kcal/mol for reaction 1b.

(13) ICR evidence and theoretical considerations show that in phenol and anisole the energetically preferred site of protonation is at the para position of the ring, rather than at the oxygen atom. Cf. B. S. Freiser, R. L. Woodin, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 6893 (1975); R. T. Mc Iver, Jr., W. Colling, and W. J. Hehre, in press, quoted by T. F. Wolf, J. L. Devlin, III, R. W. Taft, M. Wolfsberg, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 287 (1976).

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The Correlation of Carbenic Reactivity

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Abstract: Dual substituent parameter equations of the form $m_{CXY} = c_R\Sigma_{X,Y}\sigma_R + c_I\Sigma_{X,Y}\sigma_I + c_o$, in which m_{CXY} is the least-squares slope of log $(k_i/k_{isobutene})$ for CXY vs. log $(k_i/k_{isobutene})$ for CCl_2, correlated the olefinic selectivities of ten carbenes. Observed m_{CXY}s included: CF_2, 1.48; CFCl, 1.28; CCl_2, 1.00; CH_3SCCl, 0.91; C_6H_5CF, 0.89; C_6H_5CCl, 0.83: C_6H_5CBr, 0.70; CBr_2, 0.65; CH_3CCl, 0.50; and $BrCCOOC_2H_5$, 0.29. Special problems were encountered with $HCCOOC_2H_5$, for which *m* could not be determined at 25 °C. The comparative merits and the significance of the several correlations are discussed. A consideration of steric effects is included, and extensions to the chemistry of CH_3OCF and C_6H_5OCF are appended.

The quantitative correlation of carbenic reactivities was initiated by Hine's classic studies of haloform hydrolysis.[2] The discovery that dihalocarbenes added to alkenes[3] stimulated attempts to characterize carbenic selectivity toward alkenes; measurements of the relative reactivities[4] of CBr_2[5,6] and CCl_2[6] toward simple olefins were soon reported, and were followed quickly by analogous studies of many other carbenes.[7] These investigations showed that CCl_2, CBr_2, and numerous related species were electrophilic toward alkenes. In the absence of major steric effects, the most highly alkylated substrates were attacked most rapidly. Various renderings of the transition state for carbene-alkene addition have incorporated this finding, including the early qualitative renderings,[5,6,8] and the more sophisticated representations derived from molecular orbital calculations.[9] All assume initial attack of the carbene's vacant p orbial on the olefin's π electrons.

The first attempts to quantitatively interrelate the selectivities of carbenes involved comparisons of the abilities of CBr_2[6] and of lithium chlorocarbenoid[10] to discriminate within sets of olefinic substrates with parallel data for CCl_2. This type of linear free energy correlation became popular, so that by 1969 Skell and Cholod could cite six examples.[11] However, the carbenic selectivities had not been measured under comparable conditions; substrate set, reaction temperature, and generative methods varied; comparisons were qualitative at best, and could not be further analyzed.

A general empirical correlation of carbenic selectivity toward alkenes must consider dependence on alkene substituents, dependence on carbenic substituents, dependence on carbene multiplicity, and dependence on the method of carbene generation (i.e., whether free carbenes or carbenoids are the key intermediates). We adopted the following conventions.[12] A standard set of alkenes (tetramethylethylene, trimethylethylene, isobutene (standard alkene), *cis*- and *trans*-butene) and a standard carbene (CCl_2) were selected. Relative reactivities $(k_i/k_{isobutene})$ were measured for CXY and for CCl_2 at 25 °C, and the "carbene selectivity index", m_{CXY}, was defined as the least-squares slope of log $(k_i/k_{isobutene})_{CXY}$ vs. log $(k_i/k_{isobutene})_{CCl_2}$. Only carbenes known to be reacting as singlets[13] were included, and we endeavored to exclude carbenoids (see below).

Six m_{CXY} values were initially available, and could be correlated by a dual substituent parameter equation of the form

$$m_{CXY} = c_R\Sigma_{X,Y}\sigma_R^+ + c_I\Sigma_{X,Y}\sigma_I + c_o \qquad (1)$$

in which $\Sigma_{X,Y}$ represented the sum of the appropriate σ constants for the X and Y substituents of CXY.[14] The striking success of this correlation raised new and important questions: (1) Could additional carbenes be satisfactorily included? (2) What role did steric factors, not explicitly included in eq 1, play in carbene-alkene additions? (3) What was the predictive power of eq 1? (4) What limits did eq 1 impose on the reactivities of the carbenes which could be successfully treated? Here, we reconsider, refine, and amplify the correlation of carbenic reactivity in the light of recently determined m_{CXY} values, and within the framework constructed by these questions.

Results and Discussion

Collection and Correlation of Data for Carbenes of Moderate and Low Selectivity. From our previous study,[14] six m_{CXY} values were available: CH_3CCl, 0.50;[15] C_6H_5CBr, 0.70;[16] C_6H_5CCl, 0.83;[17] CCl_2, 1.00;[18] CFCl, 1.28;[19] and CF_2, 1.48.[20] The first three species, and CF_2, were generated by photolyses of the respective diazirines, and react as free (see below) singlet[13] carbenes. CCl_2 and CFCl were generated by alkoxide-induced α-eliminations. The freeness of CCl_2 under these conditions has been established;[21] CFCl should similarly be free (see below).

To extend the reactivity correlation, a number of additional carbenes were studied. Previously, we had shown that

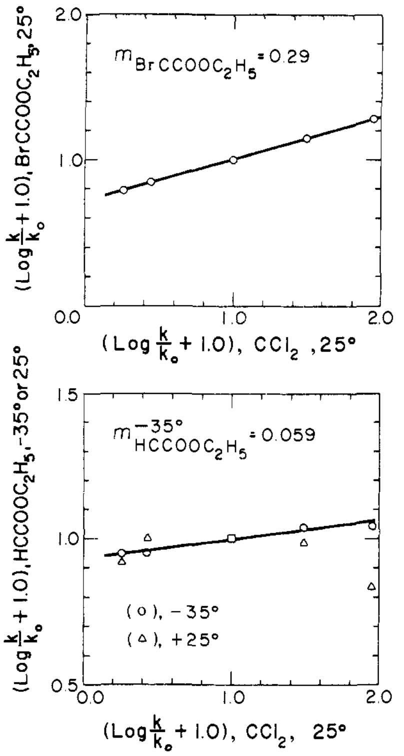


Figure 1 (above). Log $(k_i/k_0)_{BrCCOOC_2H_5}$ vs. log $(k_i/k_0)_{CCl_2}$ at 25 °C. The correlation coefficient is 0.9999; (below) log (k_i/k_0) for HCCOOC$_2$H$_5$ at −35 °C[28] (circles) and at 25 °C (triangles) vs. log (k_i/k_0) for CCl$_2$ at 25 °C. The correlation coefficient for the −35 °C data is 0.969, indicating significance at the 99% confidence level.

Table I. Relative Reactivities in Carbene-Alkene Additions at 25 °C[a]

Alkene	BrCCOOC$_2$H$_5$	HCCOOC$_2$H$_5$
Me$_2$C=CMe$_2$	1.90	0.69
Me$_2$C=CHMe[b]	1.41	0.97
Me$_2$C=CH$_2$	1.00	1.00
cis-MeCH=CHMe[b,c]	0.70	0.99
trans-MeCH=CHMe[c]	0.62	0.82

[a] Average deviations from the means of duplicate runs were within 4%, and satisfactory cross checks[7] were obtained. [b] Sum of *syn*-carboethoxy and *anti*-carboethoxy modes of addition. [c] The addition was stereospecific (>99%) with regard to alkene geometry.

Table II. Carbene Reactivity Correlations:

$$m_{CXY} = c_R\Sigma_{X,Y}\sigma_R + c_I\Sigma_{X,Y}\sigma_I + c_o$$

Eq	σ_R type[a]	c_R	c_I	c_o	f[b]
2	$\sigma_R{}^+$	−1.10	+0.53	−0.31	0.092
3	$\sigma_R{}^0$	−1.77	+0.31	−0.08	0.110
4	σ_R(BA)	−1.29	+0.29	−0.05	0.108
5	$\sigma_R{}^+$	−1.00	+0.23	0.00[c]	0.129
6	$\sigma_R{}^0$	−1.75	+0.22	0.00[c]	0.112
7	σ_R(BA)	−1.29	+0.36	0.00[c]	0.108

[a] σ values were taken from ref 30. [b] f = root mean square of the deviations of m_{CXY}s calculated by the equation/root mean square of the experimental m_{CXY}s. Correlations of acceptable precision have $f < 0.1$.[30] Correlations employing $\sigma_R{}^-$ gave very high f values and are omitted. [c] c_o was deliberately set = 0.

C$_6$H$_5$CBr and C$_6$H$_5$CCl could be generated as free carbenes from potassium *tert*-butoxide and the requisite benzal halides if 18-crown-6 was present to preclude carbenoid formation.[22] These crown ether-base-generated species had reactivities identical with those of the corresponding diazirine-photogenerated carbenes, implying that a single intermediate, the free, nonexcited, singlet[13] carbene, was involved, independent of generative method. There were, moreover, clear implications that we could determine whether other base-induced α-eliminations gave carbenes or carbenoids by measuring their olefinic selectivities in the presence and in the absence of crown ether, and that the use of KOR-18-crown-6 should make free carbenes available from halide precursors in cases where diazoalkane or diazirine precursors were unavailable.

These implications were substantiated by the generation of C$_6$H$_5$CF[23] and CH$_3$SCCl[24] from potassium *tert*-butoxide and C$_6$H$_5$CHFBr or CH$_3$SCHCl$_2$, respectively. Diazo precursors were unknown in each case. C$_6$H$_5$CF, which showed altered reactivity in the presence of 18-crown-6, was presumably a free carbene under these conditions, and a carbenoid in the absence of the crown ether.[25] CH$_3$SCCl, on the other hand, exhibited invariant reactivity toward alkenes in the presence or absence of 18-crown-6; presumably, this carbene was sufficiently stabilized by its substituents to eschew carbenoid formation even in the absence of 18-crown-6.[26] From reactivities measured in the presence of 18-crown-6 we obtained $m_{C_6H_5CF} = 0.89$ and $m_{CH_3SCCl} = 0.93$.[25]

We next reinvestigated the classic generation of CBr$_2$ from bromoform and potassium *tert*-butoxide.[5,6] There appeared to be minimal carbenoid involvement, and m_{CBr_2} (crown ether value) was determined to be 0.65.[27]

Extension of the correlation toward less selective carbenes led us to BrCCOOC$_2$H$_5$ and HCCOOC$_2$H$_5$, for which relative reactivities had been determined, but not at 25 °C.[28] We therefore redetermined these data at 25 °C, employing the usual competitive technique.[6,7] The carbenes were generated by photolyses of the respective diazo compounds (λ >300 nm); insertion products were destroyed by ozonolysis;[29] and the cyclopropane products were assayed with capillary GC (calibrated, flame ionization detector, electronic integrator). The relative reactivities thus obtained appear in Table I, normalized to $k_{isobutene} = 1.00$.

The BrCCOOC$_2$H$_5$ data readily afford $m^{25°}{}_{BrCCOOC_2H_5} = 0.29$, cf. Figure 1. However, in contrast to its behavior at −35 °C,[28] where $m_{HCCOOC_2H_5}$ is 0.059, there was *no linearity* between log $(k_i/k_0)_{HCCOOC_2H_5}$ and log $(k_i/k_0)_{CCl_2}$ at 25 °C; accordingly the value of $m^{25°}{}_{HCCOOC_2H_5}$ could not be calculated. The dramatic, temperature-dependent alteration of HCCOOC$_2$H$_5$ selectivity is displayed in Figure 1; a brief discussion will appear below.

Multiple linear regression analysis[30] of the dependence of m_{CXY} (for the ten carbenes discussed above) on σ_I and several different resonance σ parameters gave a family of equations of the form of eq 1. These are summarized in Table II. As previously observed with a more restricted set of carbenes,[14] $\sigma_R{}^+$ affords the best correlation in a three-parameter equation; cf.

$$m_{CXY} = -1.10\Sigma_{X,Y}\sigma_R{}^+ + 0.53\Sigma_{X,Y}\sigma_I - 0.31 \qquad (2)$$

Indeed, in terms of f, it gives the only "acceptable" correlation. In Table III, we display the experimental m_{CXY}s, and the m_{CXY}s calculated by the three-parameter equations, and by the best of the two-parameter equations, eq 7; also included is Δm ($m_{CXY}{}^{obsd} - m_{CXY}{}^{calcd}$) for eq 2. In Figure 2, $m_{CXY}{}^{obsd}$ and $m_{CXY}{}^{calcd}$ (according to eq 2) are graphically related. The slope of the least-squares regression line is 1.00, and the correlation coefficient is 0.971, significant at the 99.9% confidence level. The standard deviation of the residuals = 0.089; it may be seen that $m_{CBr_2}{}^{calcd}$ deviates most seriously from $m_{CBr_2}{}^{obsd}$, and from the regression line. This is discussed below. Note that eq 2 correlates the "extreme" carbenes, CF$_2$ and

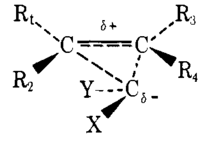
Table III. Calculated vs. Observed Carbene Selectivity Indices

Carbene	m_{CXY}^{obsd}	m_{CXY}^{calcd} from eq[a]				
		2	Δm[b]	3	4	7
CF_2	1.48	1.47	0.01	1.43	1.50	1.52
CFCl	1.28	1.22	0.06	1.22	1.21	1.22
CCl_2	1.00	0.97	0.03	1.02	0.91	0.92
CH_3SCCl	0.91[c]	d	d	0.88	0.96	0.96
C_6H_5CF	0.89	0.96	−0.07	0.90	0.95	0.94
C_6H_5CCl	0.83	0.71	0.12	0.69	0.65	0.64
C_6H_5CBr	0.70	0.64	0.06	0.62	0.60	0.58
CBr_2	0.65	0.82	−0.17	0.86	0.80	0.80
CH_3CCl	0.50	0.58	−0.08	0.65	0.61	0.59
$BrCCOOC_2H_5$	0.29	0.26	0.03	0.24	0.33	0.33

[a] See Table II for equations and their numerical designations. [b] $m_{CXY}^{obsd} - m_{CXY}^{calcd}$ for eq 2. [c] This value is an average of m_{CXY} determined in the presence (0.93) and absence (0.88) of 18-crown-6.[25] [d] See text.

$BrCCOOC_2H_5$, very well. In CXY, one anticipates direct resonance interaction between the lone pairs on X and Y and the vacant carbenic p orbital. It is therefore satisfying that the best correlation is obtained with $\sigma_R{}^+$, the resonance substituent constants intended for such situations.[30] Elimination of the floating constant, c_o, leads to poorer correlations, eq 5-7. For the best of these, eq 7, the standard deviation of the residuals is 0.10.

Discussion of Eq 2. The first question of the introduction can be answered affirmatively: additional carbenes can be correlated by eq 1. Although the inclusion of C_6H_5CF, CBr_2, and $BrCCOOC_2H_5$ has caused some loss of precision (*f* increased from 0.057[14] to 0.092 for the best correlation, eq 2, mainly due to the inclusion of CBr_2; see below), the expanded correlation is still acceptable and its significance in terms of carbenic selectivity is clear. Increasing π-electron donation *and* increasing inductive withdrawal by X and Y *both* augment electrophilic selectivity of CXY; the coefficients of $\sigma_R{}^+$ and σ_I are negative and positive, respectively.[31] The classical transition state, **1**,[5,6,8,9,14] is in accord with the correlation analysis: electrophilic selectivity is greatest when strong resonance interactions of X and Y with the carbenic center necessitate correspondingly strong π-electron donation by the olefin; electron-releasing alkyl substituents moderate the resulting accumulation of positive charge on the olefinic centers, while inductively withdrawing carbenic substituents mitigate the accumulation of negative charge on the carbenic center.



1

The correlative ability of eq 2 is currently unique. Consider the alternative quantitative treatments of carbenic reactivity, which are largely based on the Hammett equation. In most examples, a carbene is forced to choose between variously substituted styrenes; relative reactivities are calculated, and a ρ value is determined. Recent important applications include cyclopentadienylidene, $\rho = -0.76$ (σ) or -0.46 (σ^+);[33] 5-carbena-1,4-diphenyl-1,2,3-triazole, $\rho = -1.0$ (σ_p);[34] and $(CH_3)_2C{=}C{:}$, $\rho = -0.75$ (σ).[35] Earlier examples are summarized in ref 7. Although, in each case, the reactivity of the subject carbene can be characterized in terms of the sign and magnitude of ρ, comparisons with other carbenic species are necessarily qualitative because the various ρ values have generally been obtained under different conditions. Moreover, they are often satisfactorily determined by only a single kind of σ constant, which may vary from carbene to carbene.

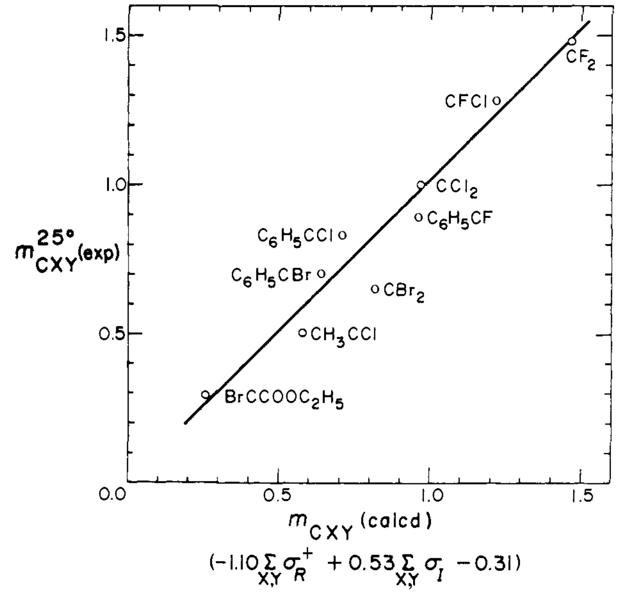


Figure 2. Slopes (m_{CXY}) of log (k_i/k_0) for CXY vs. log (k_i/k_0) for CCl_2 vs. $\sigma_R{}^+$ and σ_I; see eq 2.

In principle, if carbene generative conditions were held constant, and a single set of σ constants could be employed, an equation such as 1 should be obtainable, with ρ_{CXY} replacing m_{CXY}. In this vein, Watanabe et al.[36] have examined Si-H insertion reactions of carboethoxycarbene into aryldimethylsilanes. The ρ values for this reaction, and for the analogous insertion of CCl_2, were found to be proportional to the sums of the σ* values for the substituents of each carbene. Further generalization will require standardization of carbene generative conditions and an alternative choice of substituent constants. Kostikov, in a different approach, has correlated the selectivity of CCl_2 toward aryldienes by both the ρσ method and by the calculated π-localization energies for CCl_2 attack at the various dienic carbon atoms.[37] The latter method has not yet considered the systematic variation of carbenic substituents.

The second question of the introduction concerned the role of steric hindrance in carbene-alkene addition reactions.[38] The carbene most relevant to a discussion of eq 2 is CBr_2, for which m^{calcd} seriously deviates from the experimental value; cf. Table III. CBr_2 was initially reported to exhibit a discontinuous steric effect; i.e., it added to tetramethylethylene more slowly than to trimethylethylene,[6] but this behavior was not encountered under our standard conditions. Here, the determination of m_{CBr_2} appeared quite straightforward: we observed k_{tetra}/k_{tri}

= 4.0, and the normal log-log correlation gave $m_{CBr_2} = 0.65$, with correlation significant at the 99.9% confidence level.[27] Nevertheless, it is now clear that greater steric hindrance opposes CBr_2 as compared to CCl_2 additions: $\delta_{CBr_2}/\delta_{CCl_2} = 1.11$ for correlations of the relative reactivities of these carbenes toward $RCH{=}CH_2$ with E_s, the steric substituent constants of the alkyl groups.[27] If one arbitrarily enhances $m_{CBr_2}{}^{obsd}$ by 11%,[39] the relative steric demand of CBr_2, one obtains $m'_{CBr_2} = 0.72$, closer to $m_{CBr_2}{}^{calcd} = 0.82$.[40] In principle, steric hindrance corrections could be determined, relative to CCl_2, for all the carbenes in Table III, and these could be explicitly included in eq 2. Indeed, the point of greatest interest is not that the equation can be improved by inclusion of a steric term (see below), but that it works so well *without* the explicit inclusion of this term. At least partially, this must reflect the high reactivity of even the more selective carbenes which, with simple olefinic substrates, must lead to early, relatively "loose" transition states, in which differential steric effects are of minor importance.

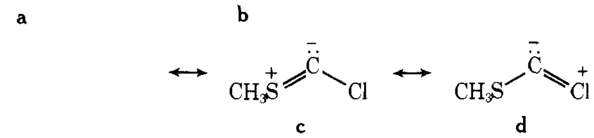
Two attempts were made to modify eq 2 by the inclusion of a steric term. Using either cyclohexane A values[41] or Charton's ν values[42] as steric substituent parameters for the carbene, we derived eq 8 and 9.

$$m_{CXY} = -0.98\Sigma_{X,Y}\sigma_R{}^+ + 0.41\Sigma_{X,Y}\sigma_I - 0.012\Sigma_{X,Y}A - 0.109 \quad (8)$$

$$m_{CXY} = -1.29\Sigma_{X,Y}\sigma_R{}^+ + 0.60\Sigma_{X,Y}\sigma_I + 0.083\Sigma_{X,Y}\nu - 0.626 \quad (9)$$

The f values for these equations are 0.084 and 0.082, respectively. The small improvement on eq 2, for which $f = 0.092$, may simply be a consequence of the addition of a new parameter. In particular, neither equation gives a very substantial improvement in $m_{CBr_2}{}^{calcd}$ (0.80 and 0.78 for eq 8 and 9, respectively, vs. 0.82 for eq 2, and 0.65 for $m_{CBr_2}{}^{obsd}$), and the coefficients of the steric terms in these equations are quite small, relative to those of the electronic terms. Presently, eq 2 seems adequate for the correlation of carbenic reactivities; there is no compelling reason for the introduction of a steric parameter.

A brief discussion of CH_3SCCl is also relevant. Using $\sigma_R{}^+(CH_3S) = -0.91$, a 1964 value,[43] $m_{CH_3S}{}^{calcd} = 1.42$; i.e., CH_3SCCl should be of selectivity comparable to CF_2 ($m_{CF_2}{}^{obsd} = 1.48$). Experimentally, however, $m_{CH_3SCCl} = 0.91$ (Table III), making it *less* selective than CCl_2. While our work was in progress, revised $\sigma_R{}^+$ values appeared,[30] in which the CH_3S substituent was reported to behave acceptably in all *but* the $\sigma_R{}^+$ parameter set.[44] Indeed, $\sigma_R{}^+(CH_3S)$ was found to range from −0.55 to −0.95, depending on reaction type.[44] Using eq 2, and $m_{CH_3SCCl}{}^{obsd} = 0.91$, we can construct an equation in which $\sigma_R{}^+(CH_3S)$ is the only unknown, and determine its value as −0.39 for the addition of CH_3SCCl to alkenes.[45] This is the least negative $\sigma_R{}^+$ value yet recorded for (CH_3S), suggesting that an adequate resonance description of the carbene, **2,** might well include such "reverse" forms as **2b,** in order to account for its poor electrophilic discrimination.[46] The lack of dominant resonance donation by CH_3S in CH_3SCCl is also suggested by the rather good correlation of $m_{CH_3SCCl}{}^{obsd}$ obtained with eq 3 and 4, which utilize $\sigma_R{}^0$ and σ_R(BA), well behaved for CH_3S; see Table III.



2

Extension of the Correlation Equation.

Extension of the Correlation Equation. The final questions posed in the introduction concerned the predictive value of equations such as 2, and whether there were limits to the carbenic reactivities which could be treated; these questions are best considered together.

Carboethoxycarbene is predicted by eq 2 to have $m = -0.30$. This clearly poor prediction is forced by the floating "constant", $c_o = -0.31$ (cf. Table II), of eq 2. The related two-parameter correlation, eq 5, gives $m_{HCCOOC_2H_5} = -0.07$, an improvement, because $m^{-35°}{}_{HCCOOC_2H_5}$ was observed to be 0.059,[28] cf. Figure 1, and m should approach zero as the temperature is raised. The difficulties are finessed, however, by the failure of $(\log k_i/k_0)^{25°}{}_{HCCOOC_2H_5}$ to be linearly related to the corresponding data for CCl_2; cf. Figure 1; $m^{25°}{}_{HCCOOC_2H_5}$ cannot be experimentally determined. Indeed the 25 °C behavior of $HCCOOC_2H_5$, relative to that of CCl_2, resembles a "broken" Hammett plot, which typically signals a change in mechanism.

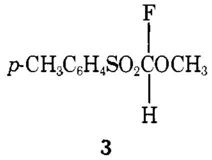
Note that the highly substituted alkenes appear less reactive toward $HCCOOC_2H_5$ than they should be. This may reflect competitive C-H insertion reactions on the part of $HCCOOC_2H_5$, which become important with tri- and tetramethylated alkenes. Having an abundance of allylic C-H bonds, and rather hindered π bonds, these alkenes suffer relatively more insertion and undergo less addition than their less substituted homologues. Because our analytical procedure selectively destroys insertion products, the observed result is a low yield of addition product from the highly substituted alkenes and, consequently, a low value of (k_i/k_0). The "change in mechanism" displayed in Figure 1 therefore suggests increasing importance of insertion, relative to addition, as increasingly methylated alkenes become the substrates for $HCCOOC_2H_5$. This problem is not encountered with $BrCCOOC_2H_5$, which gives very little C-H insertion, even with tetramethylethylene. Indeed, the carbenes of Table III do not insert appreciably into the alkenes of our standard set.

Nature therefore decrees a lower limit to the scope of the m_{CXY} correlation: carbenes which are substantially more reactive than $BrCCOOC_2H_5$, i.e., for which $m_{CXY}{}^{calcd}$ is substantially less than 0.29, will undergo too much concomitant insertion to permit determination of $m_{CXY}{}^{obsd}$.[47]

Carbenes *more selective* than CF_2 may be readily identified using eq 2; it is necessary only to select carbenic substituents for which $\sigma_R{}^+ \ll 0$. The $\sigma_R{}^+$ values[30] for CH_3O, C_6H_5O, and F are −1.02, −0.87, and −0.57, respectively, leading to $m_{CXY}{}^{calcd} = 2.22$, 1.85, and 1.74 for $C(OCH_3)_2$, CH_3OCF, and C_6H_5OCF, according to eq 2. $m_{CF_2}{}^{obsd} = 1.48$ (Table III), so that each of these carbenes is predicted to be more discriminating than CF_2 toward the standard set of alkenes.

Dimethoxycarbene need not be considered further, because it is known not to add to simple alkenes.[50] Electron donation by the methoxy substituents is so strong that little "vacant" character remains in the carbenic p orbital, and $C(OCH_3)_2$ behaves instead as a nucleophile, adding preferentially to electrophilic alkenes such as diethyl fumarate or maleate.[50,51] These results suggest that correlation equations such as eq 2 are limited to carbenes with $m_{CXY}{}^{calcd} < 2.2$.

Attention is thus focused on CH_3OCF and C_6H_5OCF. The former has been generated by photolysis of methoxyfluorodiazirine,[52] but the synthesis of this precursor is dangerous,[53] suggesting the need for an alternative. In initial experiments,[54] we treated fluorosulfone **3**[55] with KO-*t*-Bu in benzene solution,



$$p\text{-}CH_3C_6H_4SO_2\overset{F}{\underset{H}{C}}OCH_3$$

3

$CH_3OCH(SC_6H_5)_2$

4

apparently generating CH_3OCF. Cyclopropanation, however, was not observed in the presence of either tetramethylethylene or styrene. Indeed, only thiophenoxide ion has thus far been found capable of intercepting CH_3OCF, generated in this manner, with the formation of mixed thioorthoformate **4** in 30% yield. This reaction resembles the conversion of isopropoxide ion to triisopropyl orthoformate by CF_2,[57] and an analogous (though speculative) mechanism could be written. The important implication of this preliminary work is that CH_3OCF is so strongly stabilized by substituent electron donation that it is no longer sufficiently electrophilic to react with (weakly nucleophilic) alkenes in the presence of potent nucleophiles such as butoxide ion. Nonnucleophilic methods of generating CH_3OCF must be sought.

A similar impasse was encountered in the generation of C_6H_5OCF by the action of KO-*t*-Bu on α-chloro-α-fluoroanisole.[57,58] The putative carbene intermediate could not be trapped by tetramethylethylene, styrene, norbornadiene, methyl cinnamate, or methyl acrylate. Reaction with phenoxide ion did, however, afford triphenyl orthoformate;[59] a mechanism analogous to that of the CF_2 + isopropoxide reaction[57] can also be drawn here. Again, the carbene appears to be insufficiently electrophilic to react with an alkene in the presence of alkoxide ion; a nonbasic method of generation is required.

Until alternative generations of CH_3OCF and C_6H_5OCF are perfected, and the alkene addition reactions are studied, CF_2 remains the most selective carbene for which m_{CXY} is known, and $m_{CXY} \sim 1.5$ remains the upper limit for which carbene selectivity indices can be experimentally determined. Because $C(OCH_3)_2$ does add to styrene,[50] a correlation equation based on ρ values could perhaps be developed for carbenes of high m^{calcd}. However, although eq 2 holds for the additions of CXY to simple alkenes, a different interplay of resonance and inductive effects may govern the selectivity of CXY toward aryl-conjugated alkenes,[14] making it difficult to bridge the existing m_{CXY} and the potential ρ_{CXY} reactivity scales. This problem invites investigation.

Within the reactivity limits currently set by the state of the carbene chemiscry art, the family of equations represented by 1, particularly eq 2, very satisfactorily correlates a broad range of carbene-alkene reactivities, anchored at one end by the unselective $BrCCOOC_2H_5$ (for which $k_{\text{tetramethylethylene}}/k_{trans\text{-butene}} = 3.1$), and at the other end by the highly selective CF_2 (for which the same ratio is 220). Moreover, acceptable correlation can be effected without explicit consideration of differential steric effects, although these do exist and can be significant in certain cases (e.g., CBr_2). Finally, equations such as 2 can be easily used to predict the selectivity of unknown carbenes, guiding research and spurring synthetic efforts.

Experimental Section

Calculations. Coefficients for the two-parameter correlation equations (no. 5, 6 and 7, Table II) were determined on a Hewlett-Packard Model 9820A programming calculator using a program written by Professor Martha Cotter. All other calculations were done on a Wang Laboratories Model 700A programming calculator. The least-squares calculations of the m values used the "linear regression" portion of the "Statistical Package Program", 1997A/ST5. Calculations of the coefficients of eq 2-4, 8, and 9 were accomplished with a "Multiple Linear Regression Analysis Program", 1019A/ST3, written by P. Barthakur. The programs are available from Wang Laboratories, Tewksbury, Mass.

Cyclopropanes. The adducts of $BrCCOOC_2H_5$ and $HCCOOC_2H_5$ with the standard alkenes are all known compounds,[28,60] so that the experimental description will be as brief as possible.

Bromocarboethoxycarbene. A solution of ca. 100 mg of ethyl bromodiazoacetate[61] in 15 g of alkene was sealed in a Pyrex tube and irradiated for 36 h at 30 °C with 3000 Å lamps in a Rayonet photoreactor. Alkene was evaporated and cyclopropanes were isolated by GC using a 5 ft × 0.25 in. 3% SF-96 on 60/80 Chromosorb column operating at 95 °C with 80 mL/min He carrier gas. The retention times of the 1-bromo-1-carboethoxycyclopropanes, corresponding to the alkenes of Table I, were 14, 8.8, 6.1, 9.3, and 5.9 min (in the order of Table I). No separation was achieved of the syn and anti isomers of the adducts to trimethylethylene and *cis*-butene. The NMR spectra of the cyclopropanes agreed with those reported by Schöllkopf et al.[28]

Competition experiments involved the photolysis of 40–50 mg (0.2–0.3 mmol) of ethyl bromodiazoacetate in a mixture of 5–20 g (80–300 mmol) of each of the two subject alkenes. Photolytic conditions were identical with those of the preparative run, except that the temperature was maintained at 25 °C by means of a thermostated circulating water bath. After removal of the alkenes, product mixtures were ozonized[29] to ensure the absence of insertion products. Product cyclopropane ratios were determined on a Barber-Colman Series 5000 GC equipped with a 100-ft SF-96 Golay column and a (calibrated) flame ionization detector, coupled to a Varian Model 481 electronic integrator. Relative substrate reactivities were derived from the equation $k_A/k_B = (P_A/P_B)(O_B/O_A)$.[6] P_i represents the molar concentration of product cyclopropane i; O_i represents the molar concentration of the corresponding initial alkene. The average reactivities of each substrate, relative to isobutene, appear in Table I, normalized to an isobutene standard. Experiments were duplicated, and average deviations from the mean values were all <4%. Cross-check experiments[7] were performed. From the measured relative reactivities toward tetramethylethylene of *cis*-butene (2.72) and *trans*-butene (3.08), their calculated relative reactivity is 1.13. The experimental value was 1.13. Similarly, the calculated value for trimethylethylene vs. isobutene (shown in Table I) is 1.41. The observed value (single experiment) was 1.46.

Carboethoxycarbene. Adducts of tetramethylethylene and trimethylethylene were prepared by adding 1.0 g (8.75 mmol) of ethyl diazoacetate (Aldrich Chemical Co.) to 3.0 g (35–43 mmol) of alkene, containing 0.1 g of anhydrous $CuSO_4$, at 65–70 °C, with stirring. The addition to tetramethylethylene was done in a three-neck flask fitted with a reflux condenser; the addition to trimethylethylene required a pressure tube fitted with a side arm to contain the diazo compound. Vigorous nitrogen evalution occurred during the additions. Filtration, removal of alkene, and GC isolation (Carbowax 20M and SF-96, respectively) afforded the carboethoxycarbene adducts[28,60] in 75 and 50% yields, respectively. Structures were verified by appropriate NMR spectra. The *syn*- and *anti*-carboethoxy adducts of trimethylethylene were not separated.

Adducts of carboethoxycarbene and isobutene, *cis*-butene, and *trans*-butene were prepared by photolysis of 0.5 g (4.38 mmol) of ethyl diazoacetate in 5.0 g (89.2 mmol) of alkene using a Rayonet photoreactor equipped with 16 RPR 3000 Å lamps. Samples were sealed in Pyrex pressure tubes, and photolyses were continued for 24–48 h. Reaction product mixtures were diluted with 5 mL of methanol, alkenes were allowed to evaporate, and the resulting methanolic solutions were ozonized at −78 °C, until the uptake of ozone ceased. Ether was added and the resulting solutions were washed with 3 × 10 mL of saturated aqueous $NaHSO_3$ solution. Drying and stripping of the ethereal phases gave 15–20% yields of the appropriate cyclopropanes, which were isolated by GC (Carbowax 20M). Consonant NMR spectra were obtained.

Competition experiments involved the photolysis, for 12 h, of 100 mg (0.875 mmol) of ethyl diazoacetate in binary mixtures of 1–4 g of each alkene. Photolytic conditions, workup procedures,[62] and data analysis were identical with those described for $BrCCOOC_2H_5$. Note that alkenes were removed by careful distillation, after the photolyses, to prevent inadvertent fractionation of volatile products. Mean relative reactivities are recorded in Table I. Cross-check experiments[7] were performed. From the measured relative reactivities[63] toward isobutene of tetramethylethylene (0.836) and trimethylethylene (1.08), their calculated relative reactivity is 0.774. The experimental value[63] was 0.758. From the measured relative reactivities[63] toward isobutene of *cis*-butene (0.834) and *trans*-butene (0.855) their calculated relative reactivity is 0.975. The experimental value[63] was 0.963.

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