quantities. With 9:1 butadiene–isoprene, butadiene dimerization also gave (*E,E*)-1,3,6-octatriene (71%) as the only product.

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The Characterization of Carbene Selectivity. Applications to Difluorocarbene

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Abstract: By means of the dual substituent parameter equation, $m_{CXY} = -0.94\ \Sigma_{X,Y}\ \sigma_R^+ + 0.69\ \Sigma_{X,Y}\ \sigma_I - 0.27$ 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, the olefinic selectivity of six carbenes could be mutually correlated. Included was CF_2, $m = 1.48$. A Hammett correlation of the relative rates of addition of CF_2 to substituted styrenes (benzene, 80°) gave $\rho = -0.57$. The significance of these correlations is discussed.

Two quantitative treatments of the selectivity of carbenes toward olefins are currently in use. (1) A carbene is allowed to discriminate between variously substituted styrenes; relative reactivities are calculated, and a Hammett analysis then affords a ρ value for the carbene–olefin addition reaction. (2) Relative reactivities are determined for the addition of a carbene to each of a set of alkenes (which differ in degree or pattern of alkylation at the olefinic carbon atoms). The ability of the carbene to discriminate between the alkenes is then quantitatively compared with that of a "standard carbene" (or other electrophilic reagent) over the same set of alkenes. We have reviewed applications of these methods through 1972.[3] More recent noteworthy examples include Schöllkopf's study of carboethoxycarbene and bromocarboethoxycarbene,[4] and Kostikov's work with CCl_2.[5]

Interpretation of the resulting carbenic "selectivities" is difficult. Much attention has been given to the role of the structure of the olefinic substrate in the carbene addition reaction.[3] A crucial problem, however, is the correlation of carbenic selectivity with carbenic *identity; i.e.*, how does the selectivity of CXY vary with X and Y? Qualitative discussions abound in the literature,[3] but *quantitative* treatments are essentially nonexistent. The problem could be solved if either of the above measures of carbenic selectivity could be quantitatively related to electronic parameters characteristic of X and Y.

Initially, we employed a standard set of olefinic substrates[6] and defined a carbene selectivity index, m_{CXY}, as the least-squares slope of log $(k_i/k_{isobutene})$ for CXY *vs.* log $(k_i/k_{isobutene})$ for CCl_2.[3,7] The concept of a carbene selectivity index was not new; similar descriptors had previously been employed.[3,7,8] However, we pointed out the existence of a "fair linearity" between the m values of four chlorocarbenes, CXCl, and σ_R^+ of X. We suggested that, within this limited set of carbenes, selectivity toward alkenes was governed by the ability of X to donate electrons by resonance to the (singlet) carbene's vacant p orbital.[7]

Subsequent attempts to extend this treatment to include the selectivity of CF_2 failed.[9] Strongly curved correlations were obtained, with CF_2 at the apogee. CF_2 seemed to be *less* selective than expected, based on the behavior of the other, less resonance-stabilized carbenes.

This latter observation was interesting, in view of Jefford's report of apparent [2 + 2 + 2] cycloadditions of CF_2 and CFCl to norbornadiene.[10] It was suggested that these reactions might represent "engagement of the sp^2 orbital (nucleophilic attack)" of the carbenes.[10] We considered this possibility unlikely, because, although the selectivities of CF_2[11] and CFCl[12] toward olefins had not been as extensively studied as had that of CCl_2,[3,13] there was evidence of their electrophilic behavior toward simple alkenes.[3,11,12]

Our active interest in the analysis of carbenic selectivity, our concern with the selectivity of CF_2,[14] and the publication of Jefford's reports[10] all combined to lend a sense of ur-

gency to further work in the area of carbene selectivity correlations. This has now led us to a *new* correlation of the olefinic selectivity of CXY with resonance and inductive parameters of X and Y. The new correlation appears to be widely applicable, and it generates an holistic and satisfying picture of the transition state for the carbene olefin addition reaction.

Results and Discussion

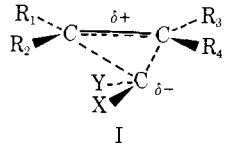
It is clear that we were arbitrary in relating m values only to the resonance parameters of the carbenic substituents.[7,9] If we include the appropriate *inductive* parameters, we at once obtain a relationship of much broader applicability.

As before, we select a standard set of olefinic substrates[6] and define the carbene selectivity index, m_{CXY}, as the least-squares slope of log ($k_i/k_{isobutene}$) for CXY *vs.* log ($k_i/k_{isobutene}$) for CCl_2, with all data taken at 25°. Relative to CCl_2, increasing m_{CXY} reflects increasing electrophilic selectivity of CXY. With a dual substituent parameter equation,[15] we can now correlate the selectivity indices of *all* "free,"[3] disubstituted carbenes for which suitable data are presently available, *including* CF_2.

Thus, m_{CXY}[25°] values are: CH_3CCl, 0.50;[16] C_6H_5CBr, 0.70;[17] C_6H_5CCl, 0.83;[18] CCl_2, 1.00;[19] CFCl, 1.28;[21] and CF_2, 1.48.[22] Multiple linear regression analysis of the dependence of m_{CXY} on σ_R^+ and σ_I constants[15] gives eq 1, in which $\Sigma_{X,Y}$ represents the *sum* of the appropriate σ constants for X and Y substituents of CXY. The variables of eq 1 are graphically related in Figure 1a. The slope of the least-squares line is 1.00, and the correlation coefficient (r) is 0.98; the correlation is significant at the 99.9% confidence level. Moreover, f,[15] the root-mean-square of the deviations/the root-mean-square of the m's, is 0.057. Correlations of good precision have $f \leq 0.1$.[15,23]

$$m_{CXY} = -0.94\Sigma_{X,Y}\sigma_R^+ + 0.69\Sigma_{X,Y}\sigma_I - 0.27 \quad (1)$$

Equation 1 correlates the selectivity indices of CXY as a blend of polar (I) and π-delocalization (R) effects. We do not yet consider it definitive because we lack m_{CXY} with X or Y = OCH_3, CN, and $COOC_2H_5$.[24] Nevertheless, we can presently observe the following. (1) The olefinic selectivity of CF_2 is precisely correlated with that of other, less strongly π-stabilized carbenes, and it is strongly electrophilic. (2) Increasing π-electron donation *and* increasing inductive withdrawal (by X and Y) *both* enhance the electrophilic selectivity of CXY; *i.e.*, the coefficients of σ_R^+ and σ_I are negative and positive, respectively. (3) Resonance and inductive contributions are comparably important; the coefficients are of similar magnitude. The first point is clearly relevant to the question of CF_2 "nucleophilicity".[10] The second and third observations evoke a transition state, I,[25] for the carbene olefin addition reaction in which 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.*



I

The latter point follows naturally from eq 1, and our treatment is the first which explicitly considers the interaction of the partial negative charge on the carbenic carbon atom of I with the carbenic substituents X and Y. The correspondence of eq 1 to the pictorial representation, I, seems to be complete and satisfying. We believe that eq 1 is capable of *correlating and predicting* the olefinic selectivities of many other carbenes, and we are studying this possibility.

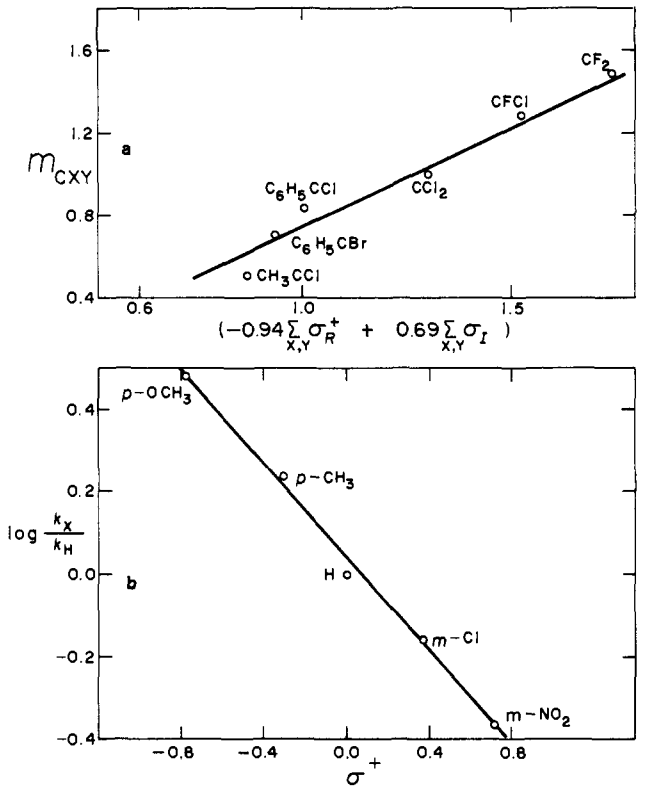


Figure 1. (a) Slopes (m_{CXY}) of log (k/k_0) for CXY *vs.* log (k/k_0) for CCl_2 *vs.* σ_R^+ *and* σ_I; see eq 1. (b) Plot of log (k_X/k_H) *vs.* σ^+ for the addition of CF_2 to substituted styrenes.

To further quantitatively characterize the selectivity of CF_2, the carbene was generated from $C_6H_5HgCF_3$ and NaI[26] (benzene, 80°) and added to $ArCH{=}CH_2$ in ~70% yields. The difluorocyclopropane products were purified by gc, and characterized by ^1H and ^{19}F nmr spectra and by elemental analysis or exact mass determinations. Relative substrate reactivities toward CF_2 were determined by competition experiments against styrene at 80° giving $k_{ArCH=CH_2}/k_{PhCH=CH_2}$. As a function of Ar, the reactivities were: p-$CH_3OC_6H_4$, 3.00; p-$CH_3C_6H_4$, 1.72; C_6H_5, 1.00; m-ClC_6H_4, 0.694; m-$O_2NC_6H_4$, 0.429.[27]

Figure 1b is a Hammett correlation of the data with σ_p^+ or σ_m, as appropriate; the least-squares ρ is −0.57, r = 0.998.[28,29] Here, again, CF_2 is an electrophile; no suggestion of nucleophilic selectivity can be detected. Note, however, that the reactivity "spread" is small ($k_{p\text{-}CH_3OC_6H_4CH=CH_2}/k_{m\text{-}O_2NC_6H_4CH=CH_2}$ = 7.0); nucleophilic selectivity toward olefins more electrophilic than m-nitrostyrene is certainly not precluded. Indeed, Hammett analysis of CCl_2 additions to p-substituted styrenes gave ρ = −0.62(σ_p^+),[30] suggesting that the electrophilic selectivity of CF_2, relative to CCl_2, decreases as the substrate set changes from alkylethylenes (m_{CF_2}/m_{CCl_2} = 1.48 at 25°) to styrenes (ρ_{CF_2}/ρ_{CCl_2} = 0.92 at 80°).

This, in turn, implies that the transition state for the addition of CX_2 to styrene significantly differs from I (R_i = alkyl only). Presumably, the charge distributions are quite different, and an attempt to correlate ρ_{CXY} with σ_R^+ and σ_I of X and Y would require coefficients other than those employed in eq 1. Expressed another way, whereas eq 1 holds for the additions of CXY to simple alkenes, a differ-

Table I. ^{19}F Nmr Data for 1,1-Difluoro-2-arylcyclopropanes[a]

Aryl substituent	J_{FF}	ϕ^{*} [b]	J_{HF}[c]	J_{HF}[d]	ϕ^{*} [e]	J_{HF}[c]	J_{HF}[d]
p-CH_3O	155.8	143.30	12.0	5.0	126.42	13.1	4.5
p-CH_3	156.3	143.36	11.7	4.7	126.17	12.0	4.5
(H)	158.0	143.32	11.3	5.0	125.96	12.4	4.7
m-Cl	158.0	143.07	12.2	5.6	126.20	11.7	4.5
m-NO_2	158.0	143.02	12.2	5.6	126.48	12.0	4.1

[a] Spectra were determined on a Varian T-60 instrument operated at 56.4 MHz. Samples were dissolved in a solvent composed of 75% CCl_4, 15% $CFCl_3$, 5% Me_4Si, and 5% octafluorocyclobutane, as an internal standard. Chemical shifts (ϕ^{*}) are reported in parts per million *upfield* from the primary standard, $CFCl_3$. On this scale, $\phi^{*}_{C_4F_8}$ is 134.92 ppm.[34] *J* values are in hertz. All spectra were very similar in appearance. [b] F syn to aryl;[35] appears as a doublet of "quartets."[36] [c] Syn-vic coupling.[37] [d] Anti-vic coupling.[37] [e] F anti to aryl;[35] appears as a doublet of "triplets." Each member of the triplets is a doublet.

ent interplay of resonance and inductive effects governs the selectivity of CXY toward aryl-conjugated alkenes.

Experimental Section

Calculations. All calculations were done on a Wang Laboratories Model 700A programming calculator. The least-squares calculations of the *m* and *ρ* values used the "Linear Regression" portion of the "Statistical Package Program", 1997A/ST5. Calculation of the coefficients of eq 1 was accomplished with a "Multiple Linear Regression Analysis Program", 1019A/ST3, written by P. Barthakur. The programs are available from Wang Laboratories, Tewksbury, Mass.

Synthesis of 1,1-Difluoro-2-arylcyclopropanes. Phenyltrifluoromethylmercury was obtained by literature methods,[26] and had mp (uncorr) 141–142° (lit.[26] 141–143°). The styrene substrates were all commercial samples and were freshly distilled before use. Distilled samples were stabilized by the addition of 0.1% of hydroquinone. The suppliers were: styrene, Matheson Coleman and Bell; *p*-methoxystyrene, City Chemical Co.; *p*-methylstyrene and *m*-chlorostyrene, Aldrich; and *m*-nitrostyrene, Pfaltz and Bauer.

In the general procedure, 330 mg (0.95 mmol) of phenyltrifluoromethylmercury and 450 mg (3.0 mmol) of dried sodium iodide [12 hr, 150° (0.1 mm)] were contained in a 10 ml-flask. A solution of 3.0 mmol of the appropriate styrene in 1 ml of benzene was forced by nitrogen pressure through a 3 × 0.5 cm column of alumina directly into the reaction flask. The column was flushed with 3 ml of benzene, which was similarly forced into the reaction flask. The flask was fitted with a reflux condenser; its atmosphere was exchanged four times against nitrogen ($p_{min} \sim 10$ mm), and it was then lowered into a preheated oil bath (80–85°). After 15–20 hr of stirring and reflux, under N_2, the reaction mixture was cooled and filtered. The filtrate was stripped of solvent, and the product cyclopropane was purified by gas chromatography (gc). Yields in all cases were ~70%, as estimated by gc analysis of crude reaction mixtures.

1,1-Difluoro-2-*p*-anisylcyclopropane. The compound had a retention time of 17.1 min on a 8 ft × 0.25 in. 10% SE-30 on 80–100 GCR column at 145°, He flow, 75 ml/min. The ^1H nmr spectrum[31] showed 7.2–6.6 (m, 4 H, aryl), 3.66 (s, 3 H, methoxy), 2.7–2.3 (m, 1 H, benzylic), and 1.95–1.13 (m, 2 H, cyclopropyl CH_2). The ^{19}F nmr spectrum is summarized in Table I.

Anal. Calcd for $C_{10}H_{10}OF_2$: C, 65.2; H, 5.44. Found: C, 65.2; H, 5.47.[32]

1,1-Difluoro-2-*p*-tolylcyclopropane. The compound had a retention time of 12 min (on the SE-30 column described above) at 130°, He flow, 75 ml/min. The ^1H nmr spectrum showed 6.97 (s, 4 H, aryl), 2.83–2.47 (m, 1 H, benzylic), 2.23 (s, 3 H, methyl), and 1.93–1.13 (m, 2 H, cyclopropyl CH_2). The ^{19}F nmr spectrum is summarized in Table I.

Anal. Calcd for $C_{10}H_{10}F_2$: C, 71.4; H, 5.95. Found: C, 71.2; H, 6.03.

1,1-Difluoro-2-*m*-chlorophenylcyclopropane. The compound had a retention time of 11.3 min on a 12 ft × 0.25 in. 10% SE-30 on 45–60 GCR column at 150°, He flow, 70 ml/min. The ^1H nmr spectrum showed 7.10 (m, 4 H, aryl), 2.90–2.35 (m, 1 H, benzylic), and 2.05–1.22 (m, 2 H, cyclopropyl CH_2). See Table I for the ^{19}F nmr spectrum.

Anal. Calcd for $C_9H_7ClF_2$: C, 57.3; H, 3.72. Found: C, 57.0; H, 3.67.

1,1-Difluoro-2-*m*-nitrophenylcyclopropane. The compound had a retention time of 20.1 min on a 5 ft × 0.25 in. 15% SE-30 on 45–60 GCR column at 145°, He flow, 80 ml/min. The product solidified upon collection, mp (uncorr) 43–44°. The ^1H nmr spectrum showed 8.0 and 7.5 (m's, 2 H each, aryl), 3.08–2.55 (m, 1 H, benzylic), and 2.19–1.39 (m, 2 H, cyclopropyl CH_2); *m/e* (calcd for $C_9H_7O_2NF_2$, 199.044) 199.042. The ^{19}F nmr spectrum appears in Table I.

1,1-Difluoro-2-phenylcyclopropane. Some properties of this compound have been described by Seyferth.[33] The ^1H nmr spectrum showed 7.1 (s, 5 H, phenyl), 2.88–2.33 (m, 1 H, benzylic), and 1.97–1.17 (m, 2 H, cyclopropyl CH_2). See Table I for the ^{19}F nmr spectrum.

Competition Experiments. These were carried out on binary mixtures of styrenes exactly as described for the syntheses, described above. The ratios of reactants were 1 equiv of phenyltrifluoromethylmercury, 5–10 equiv of NaI, ~10 equiv each of the two styrene substrates, and 4 ml of benzene. Product cyclopropane ratios were determined on a Barber-Colman Series 5000 gas chromatograph equipped with a 100 ft Carbowax K1540 Golay column and a (calibrated) flame ionization detector, coupled to a Varian Model 481 electronic integrator. Relative substrate reactivities were derived from the equation: $k_A/k_B = (P_A/P_B)(O_B/O_A)$.[38] P_i represents the molar concentration of product cyclopropane i; O_i represents the molar concentration of the corresponding initial styrene. The average reactivities of each substrate, relative to styrene itself, are reported in the text. Experiments were duplicated, and average deviations from the mean values were all <3%.

Cross-check experiments[38] were performed. From the measured relative reactivities toward styrene of *p*-methoxystyrene (3.00) and *p*-methylstyrene (1.72), their mutual calculated relative reactivity is 1.74. The experimental value was 1.78. Similarly, the calculated relative reactivity for *m*-chlorostyrene *vs.* *m*-nitrostyrene is 1.62; the experimental value was 1.54.

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Excited State Interactions and Decay Routes in Bichromophoric Systems. Nonconjugated Phenyl Ketones[1]

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Abstract: The photoreactivity of a number of β-phenyl ketones possessing γ hydrogens has been investigated. In contrast to simple aliphatic ketones, these compounds undergo the type II photoelimination exclusively from the singlet, and in general this is the only significant photoreaction. Biacetyl and *cis*-1,3-pentadiene quenching were employed to determine singlet and triplet lifetimes and intersystem crossing yields, and thus rate parameters for the decay pathways in these compounds. Since both rates of the type II process and intersystem crossing are sensitive to substitution at phenyl, we infer that there is significant coupling between the two chromophores in the excited singlet state. Studies on somewhat geometrically restricted β-phenyl ketones indicate that coupling occurs through space rather than by a through-bond mechanism. Triplet states of these compounds have somewhat shorter lifetimes than those of typical aliphatic ketones but are, in contrast, completely unreactive in the type II process.

The photoreactivity of systems containing formally nonconjugated chromophores has been the subject of many recent investigations.[3] Among the processes which have been frequently observed are efficient intramolecular transfer of excitation, as evidenced by emission spectra and chemical reactions such as cis-trans isomerization,[4-11] intramolecular exciplex and excimer formation,[12-14] as well as reactions such as intramolecular cycloadditions.[3,15,16] One of the major questions that has not yet been satisfactorily resolved concerns the occurrence of modified excited states produced by interaction of dissimilar but energetically low-lying chromophores; such interactions occurring either by orbital overlap[17] or by through-bond coupling[18-20] have been the subject of both theoretical and spectroscopic investigation.

The present paper is concerned with the photochemical reactivity of some formally nonconjugated phenyl-carbonyl compounds. Since both simple aromatic compounds and aliphatic ketones, as well as the conjugated aryl ketones, have been rather extensively studied and their excited states fairly well characterized, it appeared likely that an investigation of systems with formally nonconjugated aromatic and carbonyl chromophores might readily reveal any excited-state interactions and permit their elucidation. Although both excited singlet and triplet states of aliphatic carbonyl compounds are lower in energy than those of most simple monocyclic aromatics, the energy spacing is small, particularly between triplet states such that considerable excitation migration or excited-state interaction might be anticipated. An attractive reaction for investigation of interactions between chromophores in nonconjugated phenyl ketones appeared to be the Norrish type II intramolecular photoelimination. This reaction, which has been extensively studied,[21] occurs fairly generally and with high efficiency for ketones having a γ C–H bond and lowest lying n,π^* states. It has been previously shown that aliphatic ketones undergo the type II process from both singlet and triplet excited states.[22,23] Conjugated aromatic ketones react only from triplet states, presumably because rapid intersystem crossing deactivates the singlet before it can react. For phenyl ketones, the reaction is subject to strong substituent effects which have been attributed to mixing of ^{3}n,π^* and $^3\pi,\pi^*$ states.[21,24]

Our preliminary investigations[25] of nonconjugated phenyl ketones included a study of the type II photoelimination in 4-methyl-4-phenyl-2-pentanone (MPP) (**1**) in which the carbonyl and phenyl chromophores are separated by a two-