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(41) Just as the virtual sameness of $k_3{}^{OH}/k_{-1}$ in 60% dioxane, for the reactions of piperidine with 2,4-dinitroanisole and with 2,4-dinitrophenyl phenyl ether, showed that $k_4/k_{-3p} \gg 1$,[40] the considerably lower $k_3{}^{OH}/k_{-1}$ ratio for 2,4-dinitroanisole compared to 2,4-dinitrophenyl phenyl ether in 10% dioxane further supports the conclusion that a borderline mechanism operates due to $k_4/k_{-3p} \sim 1$ or < 1.
(42) This interpretation requires a plot of k_A vs. piperidine concentration to be curvilinear because of an increase in k_{-3p}. Whether the slight curvature in our plot (not shown) is real or whether the plot should rather be considered to be a straight line within experimental error is difficult to decide. In any event, if the plateau region ($k_4/k_{-3p} \ll 1$) has already been approached, the curvature would be slight and the plot could give the appearance of linearity.
(43) An interpretation of this small effect in terms of pipH$^+$ catalysis of methoxide ion departure (SB–GA) is a possibility; however, it is then difficult to rationalize the total absence of such an effect in 60% dioxane, where the pK difference between pipH$^+$ and MeOH is more favorable for such a mechanism.
(44) The fact that k_A is independent of the buffer ratio at amine concentrations ≥ 0.01 M, i.e., when the plateau is reached (Figure 1), indicates that $k_4/k_{-3p} \gg 1$ and not just > 1.
(45) The importance of steric hindrance of resonance can be appreciated by comparing the pK_a of *N*-methyl-2,4-dinitroanilinium ion (p$K_a = -4.8$)[46] with that of *N,N*-dimethyl-2,4-dinitroanilinium ion (p$K_a = -1.0$).[36]
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Aromatic Substitution in the Gas Phase. Predominant O-Alkylation in the Attack of t-$C_4H_9^+$ Ions to Anisole

Marina Attinà, Fulvio Cacace,* Giovanna Ciranni, and Pierluigi Giacomello

Contribution from the University of Rome, 00100 Rome, Italy. *Received October 1, 1976*

Abstract: The reaction of anisole with t-$C_4H_9^+$ ions, obtained in the dilute gas state from the γ-radiolysis of neopentane, yields exclusively *o*- and *p*-*tert*-butylanisole. Both the reactivity of anisole relative to toluene and the isomeric distribution of its alkylated products depend markedly on the composition, and especially on the pressure, of the gaseous reaction environment. The apparent $k_{\text{anisole}}:k_{\text{toluene}}$ ratio increases from 0.8, in neat neopentane at 720 Torr, to 4-5 in neopentane at 20 Torr containing a few mol % of a gaseous base, e.g., NH_3. Concurrently, the ½ ortho:para ratio decreases from 1.3 at 720 Torr to <0.2 at 20 Torr. These results, and the effects of gaseous additives, including NH_3, $(CH_3)_3N$, and $(CH_3)_2O$, are consistent with a mechanism involving kinetically predominant O-alkylation of anisole, and subsequent isomerization of the excited dialkylaryloxonium ions to thermodynamically more stable para-alkylated arenium ions. The *substrate* and *positional* selectivity of the gas-phase *tert*-butylation, and the mechanism of isomerization, involving intermolecular alkylation of the para position of anisole by the dialkylaryloxonium ion, are discussed and compared with the gas-phase data concerning *tert*-butylation of phenol, and with those of related alkylation reactions occurring in solution.

In the preceding paper of this series[1] the gas-phase attack of t-$C_4H_9^+$ ions to phenol was shown to occur predominantly at the n-type nucleophilic center of the ambident substrate, leading to kinetically predominant O-alkylation.

The present paper reports the extension of the study to anisole, which represents a particularly interesting substrate, since the dialkylaryloxonium ion formed from the t-$C_4H_9^+$ attack to the oxygen atom cannot collapse into isolable alkylation products without some kind of isomerization to a C-substituted arenium ion.

Consequently, the alkylation of anisole with *tert*-butyl cations in the dilute gas state was expected to confirm, in the first place, the kinetically prevalent role of O-alkylation established for phenol,[1] and to give further information concerning the extent and the nature of the isomerization processes of the dialkylaryloxonium ion, and its alkylating ability.

Table I. Gas-Phase Competition of Anisole and Toluene for t-$C_4H_9^+$ Ions

System composition, Torr						Relative yields of products, %[b]			
						tert-Butylanisoles		*tert*-Butyltoluenes	
Neopentane	O_2	NH_3	Anisole	Toluene	$k_{anisole}/k_{toluene}$[a]	Ortho	Para	Meta	Para
720	8		0.72	0.70	0.8	71	29	7	93
720	10		1.03	1.10	0.8	74	26	7	93
720	5	2	0.65	0.62	1.5	65	35	6	94
720	5	5	0.21	0.19	1.4	69	31	5	95
720	10	*c*	1.30	1.39	1.2	61	39	7	93
720	5	5	1.20	0.28	3.1	64	36	7	93
720	5	5	1.33	1.47	1.1	70	30	6	94
720	4	17	0.62	0.42	1.9	61	39	6	94
720	7	23	0.69	0.97	1.8	62	38	6	94
720	5	*d*	0.70	0.67	1.1	71	26	6	94
720	5	5,*e*	0.92	0.66	1.0	66	34	6	94
50	4		0.38	0.31	1.8	27	73	23	77
22	4	2	0.70	0.83	3.8	15	85	35	65
20	5		0.76	0.94	2.3	24	76	34	66
20	2		0.59	0.69	2.6	18	82	34	66
20	2	2	1.08	1.26	4.0	14	86	35	65
20	2	2,*f*	0.59	0.55	5.2	14	86	40	60
20	2	2,*g*	0.42	0.58	6.2	26	74	37	63
20	2	*h*	0.32	0.23	4.4	9	91	37	63

[a] Standard deviation of the $k_{anisole}/k_{toluene}$ ratio ca. 20%. [b] Standard deviation of data ca. 10%. [c] Containing $N(CH_3)_3$, 5 Torr. [d] Containing $(CH_3)_2O$, 20 Torr. [e] Containing also $(CH_3)_2O$, 24 Torr. [f] Containing also $(CH_3)_2O$, 2 Torr. [g] Containing also $(CH_3)_2O$, 4 Torr. [h] Containing $N(CH_3)_3$, 2 Torr.

Finally, investigation of the alkylation of anisole in the gas phase could provide a simplified and unified model for related reactions occurring in solution, whose interpretation is severely hampered by the recognized[2] effects of solvation, ion pairing, and other complicating phenomena related to the reaction environment.

Experimental Section

Materials. Anisole and toluene, research grade chemicals from Merck Co., were analyzed by GLC to check the absence of alkylated products. Neopentane, oxygen, ammonia, trimethylamine, and dimethyl ether were research grade gases from Matheson Co., with a minimum purity of 99.99 mol %.

Isomeric *tert*-butylanisoles, required as gas chromatographic standards, were prepared by alkylating anisole with $(CH_3)_3CCl$, both in perchloric acid,[3] or in the presence of $AlCl_3$. The isomers formed were resolved and purified by preparative GLC over a 4-m column packed with Carbowax 20M poly(ethylene glycol), operated at 180 °C, the identity of the purified samples being checked by NMR and IR spectrometry.

Procedure. The preparation and irradiation of the gaseous samples were carried out according to experimental techniques described in detail elsewhere.[4-5]

The analysis of the irradiation products was performed with a Model 5700 A Hewlett-Packard gas chromatograph, equipped with a FID unit, using a 4-m Apiezon L grease column at 120 °C and a 4-m poly(propylene glycol) column at 130 °C.

Results

Isomeric *tert*-butylanisoles are major reaction products from the γ-irradiation of neopentane gas containing low concentrations of anisole. Their *absolute* yields, i.e., the fraction of the radiolytic *tert*-butyl cations that gives *tert*-butylanisoles, can be calculated from the known[6,7] $G_{(t\text{-}C_4H_9^+)}$ value, and are found to depend markedly on the composition of the gaseous system and the radiation dose, since anisole faces competition of other nucleophiles, either initially present in the gas, or formed from its radiolysis, for the t-$C_4H_9^+$ reagent. In neat neopentane at 720 Torr, containing 0.1 mol % of anisole, irradiated to a total dose of 2.9 Mrad, typical absolute yields of *tert*-butylanisoles amount to 5-8%, and increase with the concentration of anisole, reaching 12-15% when the irradiated gas contains 0.2 mol % of substrate, under otherwise identical conditions.[8]

Table II. Dependence of the Isomeric Composition of Products on the Pressure

System composition, Torr				Isomeric composition of *tert*-Butylanisoles,[a] %	
Neopentane	O_2	NH_3	Anisole	Ortho	Para
720	5		0.79	68	32
720	5		1.54	63	37
720	5	10	2.75	63	37
395	5		0.59	56	44
200	5		0.98	43	57
95	5		0.38	31	69
54	2		0.59	25	75
20	2		0.70	9	91
20	2	5	0.70	10	90

[a] Standard deviation of data ca. 10%.

The typical ionic character of the alkylation process is demonstrated by the sharp decrease of the yields of *tert*-butylanisoles caused by additives, such as NH_3 or $(CH_3)_3N$, that efficiently intercept[9] the t-$C_4H_9^+$ cations. As an example, the yields measured at 720 Torr are reduced to less than 2% in neopentane containing $C_6H_5OCH_3$ and NH_3 in the molar ratio of 1:3, and the formation of *tert*-butylanisoles is practically suppressed at a ratio of 1:15.

Table I illustrates competition experiments involving toluene and anisole, giving the *relative* yields of alkylated products, their isomeric composition, and the apparent $k_{anisole}:k_{toluene}$ ratios, measured at different pressures and in the presence of various additives, NH_3, $(CH_3)_3N$, and $(CH_3)_2O$. The pressure dependence of the isomeric composition of products from anisole is illustrated in Table II. Whereas the data of the tables were obtained at the constant radiation dose of 2.9 Mrad, control irradiations, carried out at 0.29 Mrad, failed to detect significant differences in the *relative* yields, reactivity ratios, and isomeric composition of products. The major features of the gas-phase *tert*-butylation can be outlined as follows. The relative rate of alkylation of anisole and toluene by $t\text{-}C_4H_9^+$ ions in neopentane at 720 Torr depends on the relative concentration of the competing substrates, as shown by the increase of the apparent $k_{\text{anisole}}:k_{\text{toluene}}$ ratio from 0.8, measured in neat neopentane containing comparable concentrations of $C_6H_5OCH_3$ and $C_6H_5CH_3$, to the value of 3.1, measured in systems containing a 4:1 excess of anisole over the arene. At 720 Torr, the relative reactivity is also slightly affected by the presence of gaseous bases (NH_3, $(CH_3)_3N$) which cause a moderate increase of the $k_{\text{anisole}}:k_{\text{toluene}}$ ratio. At low neopentane pressures, the relative reactivity of anisole appears to increase significantly, and the bases have a much more pronounced effect. The largest enhancement of the $C_6H_5OCH_3$ reactivity relative to toluene is observed, however, at the lowest pressure investigated (20 Torr) in the presence of a few Torr of dimethyl ether, which raises the apparent $k_{\text{anisole}}:k_{\text{toluene}}$ ratio to values ranging from 5.2 to 6.2 in systems containing comparable concentrations of the two substrates.

Concerning products composition, alkylation of anisole occurs only at the ortho and para positions, at a ratio depending on the pressure and the composition of the system.

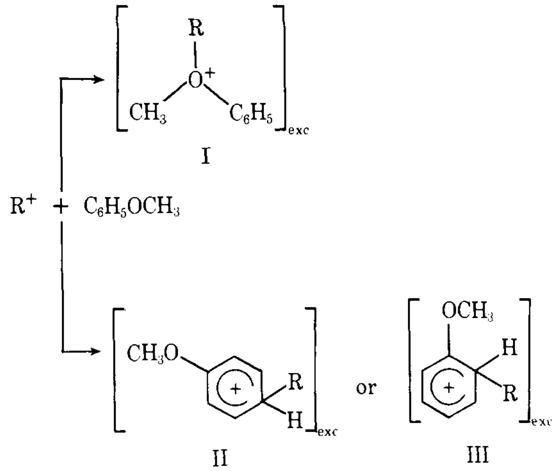
A smooth increase of the extent of para substitution with the decrease of pressure is apparent from the data of Table II. More generally, a correlation is found between the extent of para *tert*-butylation and the relative reactivity of anisole. Thus, in neat neopentane at 720 Torr, containing $C_6H_5OCH_3$ and $C_6H_5CH_3$ at comparable concentrations, the $k_{\text{anisole}}:k_{\text{toluene}}$ ratio is quite low (0.8), while the ½ ortho:para ratio reaches its maximum value, 1.3, even higher than the statistical ortho:para limit. However, in systems containing a 4:1 excess of anisole over toluene, the increase of the $k_{\text{anisole}}:k_{\text{toluene}}$ ratio to 3.1 is accompanied by a decrease of the ½ ortho:para ratio to 0.9. At low pressures, the effect even more pronounced, and the observed increase of the apparent reactivity of anisole ($k_{\text{anisole}}:k_{\text{toluene}}$ ranging from 4 to 6) involves a dramatic decrease of the ½ ortho:para ratio, down to 0.2–0.005.

Concerning toluene, only meta and para substitution take place, at rates which depend exclusively on the pressure, and are singularly unaffected by the presence of different additives, and by the $[C_6H_5OCH_3]:[C_6H_5CH_3]$ ratio. In agreement with the results of earlier investigations,[1,4,5] the data of Table I show that the percentage of *m*-*tert*-butyltoluene, a minor (5–7%) product at 720 Torr, increases regularly at the lower pressures, reaching 35–40% at 20 Torr.

Discussion

Nature and Reactivity of the Electrophile. As discussed in previous papers,[1,4,5] the reagent used in this study is the thermal $t\text{-}C_4H_9^+$ cation, formed in high yields from the radiolysis of neopentane, and completely unreactive toward the parent alkane. Both protonation and alkylation of anisole by $t\text{-}C_4H_9^+$ are energetically allowed,[10] while the reactivity of the alkyl cation toward toluene is restricted to the alkylation channel, owing to the higher PA of isobutene with respect to $C_6H_5CH_3$.[11] Hence the reactivity ratios established by the competition experiments of Table I *refer exclusively to the alkylation channel*, and clearly provide only the lower limit for the overall nucleophilic reactivity of anisole toward $t\text{-}C_4H_9^+$.

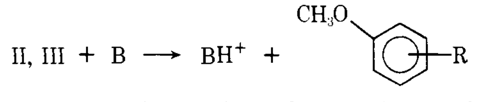
Alkylation Mechanism. It is suggested that alkylation involves the competitive attack of the *tert*-butyl cation, R^+, to the n-type and the π-type centers of the ambident substrate, giving respectively the dialkylaryloxonium ion (I) and the isomeric arenium ions II and III, excited by the exothermicity of the reaction.[12]



(1a)

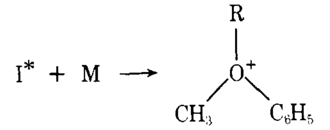
(1b)

Collisional stabilization of II and III, followed by proton transfer to a gaseous base (e.g., anisole, ammonia), provides



(2)

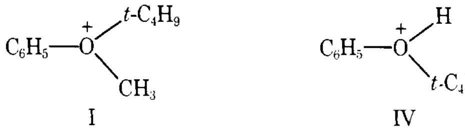
a direct route to *tert*-butylanisole. On the other hand, the excited dialkylaryloxonium ion (I), unless collisionally deactivated in the neopentane gas, tends to isomerize, via intermolecular attack to anisole, forming ring-alkylated arenium ions, in particular the para isomer (II), which eventually yields *p*-*tert*-butylanisole through reaction 2. In contrast with the



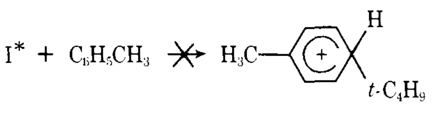
(3)

$$I^* + C_6H_5OCH_3 \rightarrow II + C_6H_5OCH_3 \qquad (4)$$

oxonium ion (IV) from the *tert*-butylation of phenol, I cannot collapse into isolable alkylation products without preliminary isomerization to arenium ions. Hence the low apparent reac-



tivity of anisole at high neopentane pressures, under conditions where collisional deactivation makes 4 a relatively slow process, can be rationalized assuming predominant formation of I, i.e., kinetically prevailing O-alkylation of anisole, in agreement with the results of the gas-phase *tert*-butylation of phenol.[1] The trend of the apparent $k_{\text{anisole}}:k_{\text{toluene}}$ ratio at low pressure indicates that I can efficiently alkylate anisole, but not toluene, which is probably due to the endothermic character of the transalkylation in contrast with the thermoneutral, or slightly exothermic, nature of process 4. With these assumptions, the higher reactivity of anisole with respect to toluene measured at low pressures can be satisfactorily rationalized on the base of the higher efficiency of isomerization processes, which accounts as well for the simultaneous increase of the extent of para substitution. In the framework of this model, a quantitative estimate of the low-pressure increase of the $k_{\text{anisole}}:k_{\text{toluene}}$ ratio, even under the restrictive assumption that the products isolated at 720 Torr derive exclusively from the direct alkylation of the ring (vide infra), leads to a ratio of O-alkylation to C-alkylation (in the kinetically significant steps of the



(5)

Cacace et al. / O-Alkylation in the Attack of t-$C_4H_9^+$ Ions to Anisole

attack) fully comparable to the ratio (ca. 8:1) measured in the gas-phase *tert*-butylation of phenol.[1]

Effect of Additives. When $(CH_3)_2O$ is present in excess over the aromatic substrate, alkylation of dimethyl ether becomes predominant, giving a high concentration of the excited trialkyloxonium ion (V), capable of attacking anisole (not toluene) at the para position, thus providing an indirect route to II,

$$R^+ + (CH_3)_2O \rightarrow \underset{V^*}{[(CH_3)_2O^+R]_{exc}} \qquad (6)$$

and consequently to *p-tert*-butylanisole. The effects of

$$[(CH_3)_2O^+R]_{exc} + C_6H_5OCH_3 \rightarrow II + (CH_3)_2O \qquad (7)$$

the $(CH_3)_2O$ additive, namely, the simultaneous increase of the reactivity of anisole relative to toluene, and of the extent of para substitution, show that the *tert*-butylation of anisole by a gaseous oxonium ion similar to I is indeed an efficient process, which occurs predominantly at the para position of $C_6H_5OCH_3$, and these observations support the role of the dialkylaryloxonium ion (I) as an alkylating agent in the suggested intermolecular isomerization (4). The effects of NH_3 and $(CH_3)_3N$ on both the relative reactivity of anisole and the isomeric composition of products, which are especially relevant at low pressure, can be explained with the fast deprotonation of the excited arenium ions, according to eq 2, leading directly to *tert*-butylanisoles, and preventing competitive reactions of II and III, either with anisole (e.g., reversible O-alkylation by the excited arenium ions), or with other nucleophiles contained in the system. On the other hand, the dialkylaryloxonium ion (I) cannot be quenched by the gaseous bases via fast deprotonation processes, and the rate of its isomerization to ring-alkylated arenium ions is apparently unaffected by NH_3 and $(CH_3)_3N$.

The Isomerization Process. Whereas the results outlined in the previous sections clearly suggest kinetically predominant O-attack, and subsequent isomerization of the dialkylaryloxonium ion to a thermodynamically more stable[13] C-alkylated cation, the evidence for a specific isomerization pathway is less conclusive. The intermolecular mechanism (4) is supported primarily by the dependence of the reactivity of anisole relative to toluene, and of the isomeric products composition, on the $[C_6H_5OCH_3]$:$[C_6H_5CH_3]$ ratio, and is consistent with the effects of the $(CH_3)_2O$ additive. Additional support for the intermolecular pathway is provided by the results of the strictly related gas-phase *tert*-butylation of phenol.[1] However, operation of the intermolecular channel does not exclude concurrent intramolecular isomerization. In other words, the question arises as to whether the isomeric composition of products measured at 720 Torr, under conditions where intermolecular isomerization becomes a slow process, reflects the selectivity of the t-$C_4H_9^+$ attack to the ring, or is there any contribution from an intramolecular alkyl shift from the oxyen to the ring. Undoubtedly, the ½ ortho:para ratio (1.3) is remarkably higher than the value measured for phenol (0.2), and represents a conspicuous singularity among gas-phase *tert*-butylation reactions, where the competition between comparably activated ortho and para positions is invariably characterized by a pronounced bias in favor of the latter. The high rate of ortho substitution from anisole cannot be explained with the higher stability of III relative to II, which is inconsistent with the low-pressure results, and must be clearly related to some specific kinetic feature of the alkylation process. Furthermore, the gas-phase reaction of $C_6H_5OC_4H_9$ with decay CT_3^+ ions[14] was reported to give appreciable yields of $CT_3O\ C_6H_4C_4H_9$ (isomeric composition was unfortunately not determined), a result that necessarily requires intramolecular migration of the alkyl group.

As a whole, these considerations suggest that intramolecular isomerization of the dialkylaryloxonium ion (I) cannot be ruled out as in the case of phenol.[1]

On the other hand, the lack of detectable meta substitution spells against the occurrence of the intramolecular 1,2 alkyl shifts within the excited arenium ions, which are operative in the case of toluene,[4] as clearly illustrated by the trend in the isomeric composition of *tert*-butyltoluenes reported in Table I.

Conclusions

The present results show that attack of t-$C_4H_9^+$ in the dilute gas state occurs predominantly at the oxygen atom of anisole, supporting the conclusions reached for the nucleophilic reactivity of phenol toward the same reagent,[4] and in agreement with independent mass spectrometric evidence.[15] The *substrate* selectivity of the *tert*-butylation, while higher than in most exothermic gas-phase substitutions, is nevertheless quite low by solution-chemistry standards, in sharp contrast with the remarkable *positional* selectivity, reflected by the kinetic predominance (over 8:1) of O-alkylation over C-alkylation, and by the lack of any detectable meta substitution. The contrast between a poor substrate discrimination and a respectable positional selectivity, that has been shown[16] to represent a typical feature of gas-phase aromatic substitutions by charged electrophiles, is fully confirmed in *tert*-butylation of anisole.

The gas-phase results reveal a remarkable degree of similarity with those of solution-chemistry studies on related alkylation processes, especially if the comparison is restricted to recent kinetic investigations carried out under carefully controlled conditions in aprotic media. Thus, Olah and Melby,[17] using CH_3SbF_6 as the electrophile in SO_2ClF, reported predominant O-alkylation of anisole at −120 °C, with a shift in favor of C-alkylation at higher temperatures, and demonstrated the alkylating ability of the dialkylaryloxonium ion intermediate, which was found to attack preferentially the para position of anisole, according to an intermolecular mechanism analogous to reaction 4. Methylation of anisole by methyl chloroformate and $AgSbF_6$ in chlorobenzene was shown[18] to involve predominant attack to oxygen, yielding a dimethylphenyloxonium ion as the major reaction intermediate, whose subsequent *intermolecular* alkylation of anisole, analogous to reaction 4, gave ring-alkylated products.

It is interesting to note that in both these solution-chemistry studies[17,18] the intervention of relatively minor *intramolecular* isomerization processes of the dialkylaryloxonium intermediates could not be excluded.

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The Correlation of Carbenic Reactivity

Robert A. Moss,* [1] Charles B. Mallon, and Chi-Tang Ho

Contribution from the Wright and Rieman Chemistry Laboratories, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903. Received December 6, 1976

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

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

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