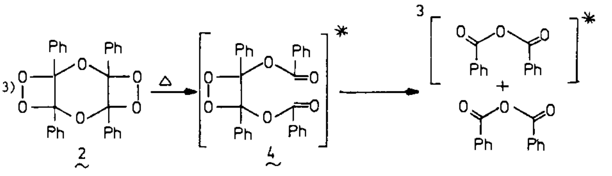
termined at 80 °C on the Mitchell-Hastings photometer, as described previously.[12] The respective ϕ^{EC} values at infinite concentration of the fluorescer, extrapolated from double reciprocal plots, were 3.48×10^{-5} einstein/mol for DPA and 1.70×10^{-3} einstein/mol for DBA. Using the fluorescence yields of DPA as 100% and DBA as 10% and a triplet-singlet energy-transfer efficiency $\phi^{ET} \sim 25\%$,[13] we estimated the triplet/singlet ratio as $\phi^T/\phi^S \sim 2000$. Thus, like the monodioxetanes,[9] the bisdioxetane **2** is also inefficient in chemienergizing a singlet excited product. In this context it is important to point out that no CIEEL[14] involvement could be observed for the bisdioxetane **2** with rubrene.

Our present results illustrate that stable bisdioxetanes can be prepared without difficulty. Their thermal behavior is quite analogous to that of the monodioxetanes,[9] affording high yields of triplet excitation. In the particular case of the bisdioxetane **2**, triplet-excited anhydride can be generated chemically. Although the details of the mechanism of chemienergization of triplet-excited anhydride product are obscure at this time, the thermal activation of 26 kcal/mol is just enough to dissociate one of the dioxetane rings in the bisdioxetane **2**. Presumably, first a triplet-excited intermediary monodioxetane **4** is formed (eq 3). The lifetime of triplet-excited **4** is expected to be short,

(eq3)



probably of the order of a vibrational period, and the triplet excitation is utilized internally to dissociate the second dioxetane ring in **4** to afford triplet-excited benzoic anhydride. We are in the process of preparing the dioxetane **4** to test these mechanistic speculations.

Recently chemienergized benzoic anhydride has been claimed[4] in the low-temperature ozonolysis of diphenylacetylene, but our bisdioxetane **2** presents a more convenient and efficient chemical source for triplet-excited anhydrides. We are actively pursuing the utility of bisdioxetanes in our chemienergization work.

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(15) (a) NIH Career Awardee, 1975–1980. (b) On study leave from the University of São Paulo, Brazil.

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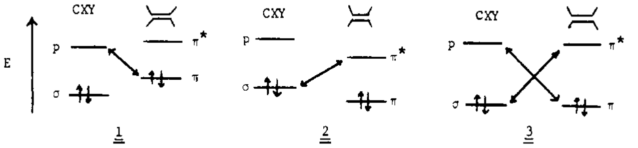
Unification of the Carbenic Selectivity Spectrum. The Ambiphilicity of Methoxychlorocarbene

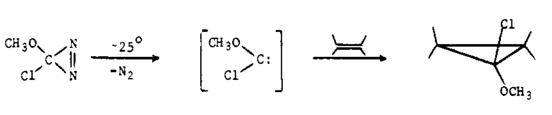
Sir:

In frontier molecular orbital (FMO) terms, the addition of a singlet carbene to an alkene involves simultaneous interactions of the vacant carbenic p orbital (LUMO) with the filled alkene π orbital (HOMO), and of the filled carbenic σ orbital (HOMO) with the vacant alkene π* orbital (LUMO).[1] This formulation easily accommodates both the familiar "electrophilic" carbenes (CCl_2, CF_2)[2] and the less common "nucleophilic" carbenes (e.g., $(CH_3O)_2C$),[3] while simultaneously suggesting the existence of ambiphilic[4] carbenes.

For example, the FMO situations for CCl_2 and CF_2 in additions to common alkenes are such that the most proximate, dominant orbital interaction is LUMO carbene/HOMO alkene[5,6] (**1**) leading to electrophilic addition. Here, net electron density is transferred from alkene to carbene in the transition state;[7] addition is facilitated by increasing the number of alkyl groups on the alkene's sp^2 carbons. Alternatively, when the HOMO-carbene/LUMO-alkene interaction is dominant (**2**) nucleophilic carbenic additions are observed,[3] in which net electron density is transferred from carbene to alkene in the transition state;[7] addition is facilitated by placing electron-attracting groups on the alkenic carbons.[3,6] Finally, if the HOMO's and LUMO's of a carbene and a simple alkene (e.g., propene) are such as to lead to comparable energy gaps for both sets of orbital interactions (**3**), then ambiphilic carbene reactivity should be demonstrable; substitution of strongly electron-donating or -withdrawing substituents on the alkene should convert situation **3** into **1** or **2**, respectively. The FMO formulation thus naturally suggests a *continuum* of carbenic behavior ranging from electrophilicity, through ambiphilicity, to nucleophilicity.



In this communication, we present the first unequivocal, experimental demonstration of an ambiphilic carbene,[4] thereby unifying the spectrum of carbenic reactivities. Methoxychlorocarbene[8] was generated by the ambient temperature thermolysis of methoxychlorodiazirine[9] (eq 1), in large excesses



(1)

of selected binary alkene mixtures. Quantitative GC analysis (calibrated tc detector) of the known[8] product cyclopropanes, coupled with standard competition reaction analysis,[2] gave the primary relative reactivites summarized in Table I. These data are normalized to a *trans*-butene standard in Table II. Satisfactory cross-check experiments[2] linked the relative reactivites of the triads $Me_2C{=}CMe_2$, $Me_2C{=}CH_2$, and *t*-Me-

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Table I. Measured Relative Reactivities of CH_3OCCl (25 ± 2 °C)

	GC conditions[a]			
olefin$_A$/olefin$_B$	column	temp, °C	k_{rel}	± av dev$_n$[b]
t-$MeCH{=}CHMe/Me_2C{=}CH_2$	A	70	0.184	0.001_5
$CH_2{=}CHCOOMe/Me_2C{=}CH_2$	A	82	5.47	0.56_6
$CH_2{=}CHCN/t$-$MeCH{=}CHMe$	A	87	54.6	2.2_4
$Me_2C{=}CMe_2/t$-$MeCH{=}CHMe$	B	37[c]	12.6	0.2_3

[a] Columns: A, 9 ft × 0.25 in. Teflon column packed with 15% SF-96 on 80/100 Chromosorb W; B, 4 ft × 0.25 in. Teflon column packed with 10% SF-96 on 90/100 Anakrom ABS. General operating conditions: injector, 162–172 °C; detector, 200–210 °C; He flow rate, 60–75 mL/min. [b] Average deviation of n experiments. [c] Special conditions: injector 55 °C; detector, 80 °C; He flow rate, 70 mL/min. Under these conditions, the adduct of CH_3OCCl and $Me_2C{=}CMe_2$ is completely stable (NMR[8] of recovered material; three experiments).

Table II. Standardized Relative Reactivities of CH_3OCCl (25 ± 2 °C)

olefin	k_{rel}[a]	olefin	k_{rel}[a]
$Me_2C{=}CMe_2$	12.6	$CH_2{=}CHCOOMe$	29.7
$Me_2C{=}CH_2$	5.43	$CH_2{=}CHCN$	54.6
t-$MeCH{=}CHMe$	1.00[b]		

[a] The associated errors are ±6–10%. [b] Standard olefin.

$CH{=}CHMe$ and $CH_2{=}CHCOOMe$, $Me_2C{=}CH_2$, and t-$MeCH{=}CHMe$. The observed value of $k_{CH_2=CHCN}/k_{Me_2C=CH_2}$ ($13.7 \pm 0.08_8$), however, was somewhat higher than the value calculated (10.0 ± 0.7) from $k_{MeCH=CHMe}/k_{Me_2C=CH_2}$ and $k_{CH_2=CHCN}/k_{MeCH=CHMe}$ (cf. Table I). The reason for this discrepancy is uncertain, but various control experiments, in the presence of added CH_3CN, ruled out solvent effect alteration of relative reactivities as a satisfactory explanation.

Previously, we showed that absolute rate constants for the thermolytic decomposition (30 °C) of methoxychlorodiazirine in $Me_2C{=}CMe_2$, $CH_2{=}CHCOOMe$, or CH_3CN displayed little solvent dependence ($k_{decomp} = 0.9\text{–}1.5 \times 10^{-4}\ s^{-1}$).[8] This is also true of decomposition in $CH_2{=}CHCN$ ($1.4 \times 10^{-4}\ s^{-1}$), indicating that the cyclopropanes of eq 1 result from additions of CH_3OCCl and not, e.g., by decomposition of an initially formed pyrazoline.

The selectivity of CH_3OCCl (Table II) is clearly indicative of its ambiphilic character: the k_{rel} sequence $Me_2C{=}CMe_2 > Me_2C{=}CH_2 > t$-$MeCH{=}CHMe$ is common to electrophilic carbenes,[2] whereas the very high reactivities toward $CH_2{=}CHCOOMe$ and $CH_2{=}CHCN$ are appropriate to a nucleophilic carbene. This dramatic selectivity pattern is currently unique[2,10] among singlet[11] carbenes, so that its demonstration serves to unify the carbenic selectivity spectrum of electrophiles, ambiphiles, and nucleophiles.

There are two ways in which the ambiphilicity of CH_3OCCl can be both anticipated and rationalized. Experimentally, the "electrophilic" selectivity of CXY toward a standard set of alkenes follows eq 2,[14] in which m_{CXY} is the least-squares slope of log $(k_i/k_{isobutene})_{CXY}$ vs. log $(k_i/k_{isobutene})_{CCl_2}$, and $\Sigma_{X,Y}$ represents the sum of the appropriate σ constants[15] for the substituents of CXY. From experiment, or calculation via eq 2,[16] we find (inter alia) that $m_{CCl_2} = 1.00$, $m_{CF_2}{}^{exptl} = 1.48$, $m_{CH_3OCCl}{}^{calcd} = 1.59$, and $m_{(CH_3O)_2C}{}^{calcd} = 2.22$. Clearly, the location of CH_3OCCl on the m scale, *between* the electrophiles[2,10] CCl_2 and CF_2[2] and the nucleophile[3] $(CH_3O)_2C$, is consistent with its transitional or ambiphilic selectivity.

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

A similar result emerges from a priori considerations. From calculated 4-31G energies (electron volts)[7] of CXY LUMO's (CCl_2, 0.31; CF_2, 1.89; CH_3OCCl, 2.46) and HOMO's (−11.44, −13.38, −10.82, respectively) and from experimental values (electron volts) of alkene π^* ($Me_2C{=}CMe_2$, 2.27; $CH_2{=}CHCN$, 0.21)[17] and π orbitals (−8.27,[18] −10.92,[19] respectively), one can derive the differential energies ($E_{CXY}{}^{LU} - E_{alk}{}^{HO}$) and ($E_{alk}{}^{LU} - E_{CXY}{}^{HO}$). For reactions of CCl_2 or CF_2, with *either* $Me_2C{=}CMe_2$ or $CH_2{=}CHCN$, the former difference is *smaller* than the latter, indicating that situation **1** applies and that these are electrophilic additions. On the other hand, although ($E_{CXY}{}^{LU} - E_{alk}{}^{HO}$) is also smaller than ($E_{alk}{}^{LU} - E_{CXY}{}^{HO}$) for reaction of CH_3OCCl with $Me_2C{=}CMe_2$ (10.73 vs. 13.09 eV),[20] the *reverse situation* (cf. **2**) is found for CH_3OCCl and $CH_2{=}CHCN$ (13.38 vs. 11.03 eV).[21] This reversal suggests that, although the additions of CH_3OCCl to $Me_2C{=}CMe_2$ or t-$MeCH{=}CHMe$ may still be characterized as electrophilic, the analogous reactions with $CH_2{=}CHCN$ or $CH_2{=}CHCOOMe$ should be considered nucleophilic. The ambiphilicity of CH_3OCCl is thus consistent with expectations based on theory.[22]

We are continuing our studies of these phenomena, searching for new ambiphilic carbenes and for "hidden ambiphilicity" in more familiar species.

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(16) Equation 2 is normalized to $m_{CCl_2} = 1.00$, giving it an electrophilic heritage. Indeed, $m_{CXY}{}^{calcd}$ for 12 carbenes, including $(CH_3O)_2C$, correlates linearly with 4-31G calculated values of $E_{CXY}{}^{LUMO}$.[7] $(CH_3O)_2C$ does not add to simple alkenes,[3] so that $m_{(CH_3O)_2C}$ is an "imaginary" selectivity index. Nevertheless, it serves to locate the *m* region in which nucleophilic carbenes reside.
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(20) An analogous situation holds for CH_3OCCl and *t*-MeCH=CHMe.
(21) An analogous situation holds for CH_3OCCl and $CH_2{=}CHCOOMe$.
(22) With $(CH_3O)_2C$ ($E^{LU} = 4.09$, $E^{HO} = -10.81$ eV),[7] $(E_{alk}{}^{LU} - E_{CXY}{}^{HO})$ is less than $(E_{CXY}{}^{LU} - E_{alk}{}^{HO})$ for $CH_2{=}CHCN$, $CH_2{=}CHCOOMe$, *t*-MeCH=CHMe, and $Me_2C{=}CH_2$ (i.e., these could be termed "nucleophilic" additions). However, with $Me_2C{=}CMe_2$, $(E_{CXY}{}^{LU} - E_{alk}{}^{HO} = 12.36$ eV) is less than $(E_{alk}{}^{LU} - E_{CXY}{}^{HO} = 13.08$ eV), suggesting that addition of $(CH_3O)_2C$ to $Me_2C{=}CMe_2$ could be characterized as "electrophilic", *if it occurred*. In fact, even the smaller, dominant differential orbital energy is still quite large (as it also is for $Me_2C{=}CH_2$ (13.0 eV) and *t*-MeCH=CHMe (12.9 eV)). Consequently, these three addition reactions do not derive enough transition-state stabilization to become energetically competitive with the alternative carbene reaction pathways which actually occur.[3]
(23) Postdoctoral Fellow on leave from the Technical University, Warsaw, Poland.

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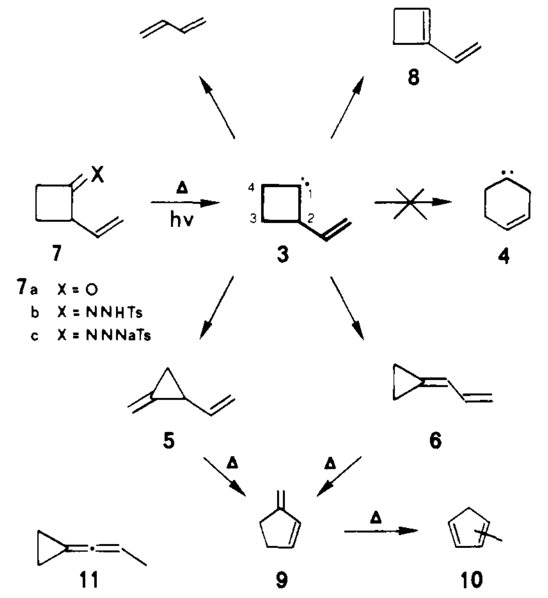
Carbene Rearrangements of 2-Vinylcyclobutylidene

Sir:

Few carbene–carbene rearrangements[1] have been reported in which the divalent carbon retains its identity. With one exception[2] all known examples involve the conversion of vinylcyclopropylidenes **1** into cyclopentenylidenes **2**.[3]

We expected that 2-vinylcyclobutylidene (**3**) would undergo an analogous carbene–carbene rearrangement.[4] Furthermore, **3** makes possible the study of two competitive pathways in the cyclobutylidene–methylenecyclopropane rearrangement of an unsymmetrically monosubstituted cyclobutylidene. Cleavage of the C_3–C_4 bond in **3** affords vinylmethylenecyclopropane (**5**),[5] whereas rupture of the C_2–C_3 bond leads to allylidenecyclopropane (**6**).[6] We find that the latter process predominates and that no carbene–carbene rearrangement (**3** → **4**) occurs.

2-Vinylcyclobutylidene (**3**) was generated either by decomposition of the dry 2-vinylcyclobutanone tosylhydrazone sodium salt (**7c**) in a flash pyrolysis system at 200 °C or by irridiation of **7c** in ethereal solution. The desired 2-vinylcyclobutanone (**7a**) was synthesized from 2-bromocyclobutanone[7] via ketalization (yield, 77%) and then introduction of the vinyl group with vinylmagnesium bromide (61%) followed by deketalization (66%). Reaction of 2-vinylcyclobutanone (**7a**)[8] with tosylhydrazide gave the corresponding tosylhydrazone **7b** in 76% yield.



The product distributions recorded in Table I indicate that 1,2-hydrogen migration amounts to <5%, affording 1-vinylcyclobutene (**8**).[9] The parent cyclobutylidene produces 20% cyclobutene.[10] Decomposition (methods a, b) of **7c** yields 1,3-butadiene in trace amounts.

Depending on the method of generation, **6** and **5** are formed in ratios 53:1, 41:1, and 23:1, respectively (Table I). It should be taken into account, however, that 3-methylenecyclopentene (**9**),[6,11] as well as the methylcyclopentadienes (**10**),[12] stems from thermal rearrangement of **5**.[13] The yield of **9** decreased when a stream of nitrogen was passed through the pyrolysis system (b), and no secondary products were observed in the photolytic experiments (c). The available kinetic data[14] suggest that **6** does not rearrange significantly under the conditions of our pyrolysis studies. Thus, **6** and **5** may be actually produced in a ratio as low as 5:1 at 200 °C.

1,3- and 1,4-cyclohexadiene, the products expected from the carbene–carbene rearrangement **3** → **4**, were not detected among the compounds obtained.[15] This observation is in stark contrast with the formation of 84% cyclopentadiene from 2-vinylcyclopropylidene (**1**).

Assuming that the divalent carbon in its singlet state approaches sp^2 hybridization, thermochemical estimates show **3** to be considerably less strained (~10–13 kcal/mol) than **1**. Conformational effects and(or) different methods of generation[16] may also be responsible for the divergent behavior of **1** and **3**.

We are currently exploring the chemistry of other vinylcyclobutylidenes and their tendency to undergo carbene–carbene rearrangements.

Acknowledgment is made to the Deutsche Forschungs-

Table I. Product Distribution from Decomposition of 7c

method[a]	6	5	8	9	10	7a	11[b]	unidentified products	total isolated yield, %
a	74.1	1.4	3.8	12.8	0.4		5.4	2.1	63
b	85.3	2.1	3.9	4.9	0.4		1.9	1.5	71
c	60.7	2.6	1.3			28.9	5.3	1.2	4[c]

[a] a, 200 °C, 10^{-3} Torr; b, 200 °C, 0.9–0.7 Torr, N_2; c, *hν*, 0 °C, ether, 6 h (125 W, Philips HPK). [b] The more NaH is used for the formation of the sodium salt **7c**, the more **11** is obtained in the reaction of **7c** (methods a, b, c). Under the reaction conditions **11** is not formed from **6**. [c] The difference in the total isolated yields (methods a, b vs. c) is due to the different methods (reaction times and workup procedures) applied.

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