Table II. Percent of Observed Products

temp, °C	4	11	5	6	7	10
-30	44	56				
-20	27	73				
-10	12	70	7	11		
0		59	17	23	≤1	
10		40	22	37	≤1	
20		8	35	45	≤1	12
25 (1 h)			39	47	≤1	13

added 57 mg (0.33 mmol) of MCPBA. The reaction mixture was allowed to stand at -40 °C for 3 h before data accumulation. In addition to small peaks for 4, MCPBA, and *m*-chlorobenzoic acid, the following signals were attributed to **11**: ^{13}C NMR (CDCl$_3$) δ 170.9, 144.0, 118.3, 81.1, 38.6, 37.6, 32.5, and 29.2.

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Registry No. 4, 33512-45-7; **5**, 108263-91-8; 6, 108296-88-4; **7**, 108296-89-5; **8**, 83720-82-5; **9**, 108296-90-8; **10**, 108296-91-9; **11**, 108296-92-0; 3,6-di-*tert*-butyl-2,3,7,7-tetramethyl-1,5-octadien-4-one, 108296-93-1; di-*tert*-butylketene, 19824-34-1; 3,6-di-*tert*-butyl-2,2,7,7-tetramethyloct-4-yn-3,6-diol, 33420-20-1.

Absolute Rate and Philicity Studies of Methoxyphenylcarbene. An Extended Range for Carbenic Ambiphilicity

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Abstract: Methoxyphenylcarbene (MeOCPh) was generated by photolysis (-10 °C) or thermolysis (25, 45 °C) of 3-methoxy-3-phenyldiazirine and added to six alkenes, affording the corresponding cyclopropanes. The substrates and their relative reactivities toward thermally generated MeOCPh at 25 °C were trimethylethylene (3.4), isobutene (10.6), *trans*-butene (1.00), 1-hexene (0.74), methyl acrylate (172), and acrylonitrile (445). Absolute addition rates were studied by laser flash photolysis, following the disappearance of MeOCPh at 290 nm. Laser flash photolysis gave no evidence for the participation of methoxyphenyldiazomethane. MeOCPh is an ambiphile with an extraordinarily strong nucleophilic component. An ab initio molecular orbital study of MeOCPh gave geometries and frontier orbital energies for the cis and trans conformers of the carbene. *trans*-MeOCPh is predicted to be ambiphilic, whereas its cis conformer is predicted to be nucleophilic in additions to the above alkenes. The very high-lying HOMO of MeOCPh is responsible for its unexpectedly pronounced nucleophilic properties.

During the past decade, several principal themes have emerged in the study of singlet carbenes that reflect a desire to more precisely quantitate and categorize the reactivity of these species toward alkenes. These themes include (1) the use of linear free energy relations and selectivity studies to define the "philicity" of the carbene;[1,2] (2) application of ab initio molecular orbital methods to calculate the carbene's HOMO and LUMO energy levels which, together with frontier molecular orbital concepts, lead to an a priori prediction of philicity;[2,3] (3) laser flash photolytic measurement of absolute rate constants and activation parameters for carbene/alkene additions;[4-6] (4) increased recognition of the role of activation entropy in determining the rates of these reactions;[6-8] and (5) development of the halodiazirine exchange reactions that make available a variety of convenient new carbene precursors.[9,10]

Four of these five themes now converge in a study of methoxyphenylcarbene (MeOCPh), the precursor of which, methoxyphenyldiazirine, was the first to be prepared by diazirine exchange.[9] Although MeOCPh is anticipated by empirical criteria to be electrophilic toward alkenes (its *calculated* selectivity index,[1,2] $m_{\mathrm{CXY}} = 1.34$, is within the currently defined "electrophilic region" of the carbene selectivity spectrum[1c,2]), ab initio calculations (see below) afford HOMO and LUMO orbital energies that lead to predictions of ambiphilicity for *trans*-MeOCPh and nucleophilicity for *cis*-MeOCPh. The conflict between these expectations stimulated the present experimental study, and the results now lead us to redefine the "border" between electrophilic and ambiphilic carbenes. Moreover, absolute rate constants were estimated for the additions of MeOCPh to electron-deficient alkenes. The resulting combination of theoretical calculations, product-based relative rate constants, and intermediate-based absolute rate

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(1) (a) Moss, R. A.; Mallon, C. B.; Ho, C.-T. *J. Am. Chem. Soc.* **1977**, *99*, 4105. (b) Moss, R. A.; Fedorynski, M.; Shieh, W.-C. *Ibid.* **1979**, *101*, 4736. (c) Moss, R. A.; Munjal, R. C. *Tetrahedron Lett.* **1979**, 4721.

(2) Review: Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58.

(3) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770.

(4) Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjal, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587.

(5) Eisenthal, K. B.; Moss, R. A.; Turro, N. J. *Science (Washington, DC)* **1984**, *225*, 1439.

(6) Moss, R. A.; Ławrynowicz, W.; Turro, N. J.; Gould, I. R.; Cha, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7028.

(7) Skell, P. S.; Cholod, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 7131.

(8) Giese, B.; Lee, W.-B.; Meister, J. *Annalen* **1980**, 725.

(9) Włostowska, J.; Moss, R. A.; Guo, W.; Chang, M. J. *Chem. Commun.* **1982**, 432.

(10) Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 2743.

Table I. Experimental Relative Reactivities of MeOCPh (25 °C)[a]

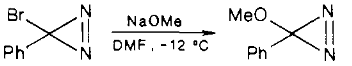
case	olefin a	olefin b	k_a/k_b[b,c]	% ad[d]
1	$Me_2C{=}CHMe$	$Me_2C{=}CH_2$	$0.32 \pm 0.02_3$	6.2
2	*trans*-$MeCH{=}CHMe$	$Me_2C{=}CH_2$	$0.094 \pm 0.004_2$	4.2
3	*n*-$C_4H_9CH{=}CH_2$	*trans*-$MeCH{=}CHMe$	$0.74 \pm 0.02_2$	2.7
4	$CH_2{=}CHCN$	$Me_2C{=}CH_2$	$41.8 \pm 3.3_2$	7.9
5	$CH_2{=}CHCOOMe$	$Me_2C{=}CH_2$	$16.2 \pm 0.2_2$	1.2

[a] The carbene was generated thermally from diazirine **1** at 25 °C. [b] Where appropriate, relative reactivities are based on composites of syn and anti isomeric cyclopropane adducts. [c] Errors are average deviations from the mean value of *n* (subscript) determinations. [d] Percent average deviation from the mean value.

measurements has made possible a much more precise description of the properties of MeOCPh than has usually been provided in previous investigations of carbenic reactivity. The results have broad implications for the relation between carbenic philicity and carbenic structure.

Results

3-Methoxy-3-phenyldiazirine (1). The diazirine precursor for MeOCPh, 3-methoxy-3-phenyldiazirine (**1**), was prepared by the exchange reaction[9] of 3-bromo-3-phenyldiazirine[10,11] with sodium methoxide in dimethylformamide (DMF) at −12 °C for about 1 h, eq 1. The yield of yellow-green **1** was ~50% after short column chromatography (silica, pentane, 0 °C). The present use of DMF as the reaction solvent is more convenient than the original[9] mixture of dimethylacetamide and hexamethylphosphoric triamide.

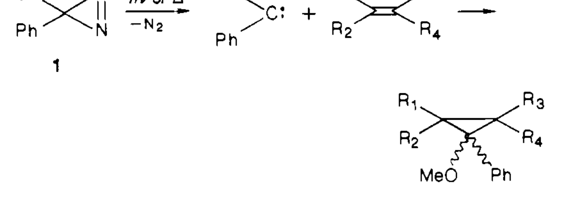


(1)

Key IR (1570 cm^{-1}, N=N) and proton NMR (δ 3.28, MeO, $CDCl_3$, −10 °C) signals of **1** have been reported.[9] The UV spectrum (Hewlett-Packard Model 8451A diode array spectrometer, 25 °C, pentane) showed λ_{max} 368 and 383 nm, in good agreement with 3-chloro- and 3-bromo-3-phenyldiazirines, reported to exhibit "broad" absorptions with $\lambda_{max} \sim 388$ nm.[11] Diazirine **1** is thermally unstable in pentane at 25 °C, $\tau_{1/2} \sim 4$–5 min. The decomposition, monitored at 379 nm, followed good first-order kinetics ($r > 0.999$), and the derived rate constants ($\times 10^3$, s^{-1}) were effectively independent of solvent polarity and of the presence of olefins or oxidants; 2.78 (pentane), 3.51 (isooctane), 4.35 (acetonitrile), 3.38 ($Me_2C{=}CHMe$, pentane), 3.58 ($CH_2{=}CHCN$, pentane), and 3.36 (*m*-chloroperbenzoic acid, pentane, CH_2Cl_2). This behavior and other experiments that appear to rule out the intermediacy of methoxyphenyldiazomethane (see below) suggest that **1** either decomposes directly to MeOCPh or transits a very unstable, short-lived diazo compound.

Diazirine **1** even appears to be unstable to several days' storage over dry ice, as judged by its failure to give reasonable yields of MeOCPh/olefin adducts after 4 days. Accordingly, **1** was prepared and used as required, with minimal storage time.

Cyclopropane Adducts. Cyclopropane **2**–**7** were prepared by photolysis (275-W GE Sunlamp, −10 °C) or thermolysis (25 or 45 °C) of diazirine **1** in excesses of trimethylethylene, isobutene, *trans*-2-butene, 1-hexene, methyl acrylate, and acrylonitrile, eq 2. The photolytic and thermolytic procedures afforded comparable yields of products. The cyclopropanes were obtained in yields of 8% (**5**) to 28% (**2**) as determined by gas chromatography (GC) or isolation. These yields are based on the *bromo*phenyldiazirine precursor of **1** and should be doubled to reflect the approximate yields in eq 2.



1

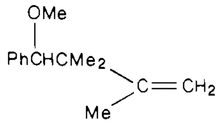
(2)

2, $R_1 = R_2 = R_3 = Me$, $R_4 = H$
3, $R_1 = R_2 = Me$, $R_3 = R_4 = H$
4, $R_1 = R_4 = Me$, $R_2 = R_3 = H$
5, $R_1 = n\text{-}C_4H_9$, $R_2 = R_3 = R_4 = H$
6, $R_1 = COOMe$, $R_2 = R_3 = R_4 = H$
7, $R_1 = CN$; $R_2 = R_3 = R_4 = H$

The new adducts (**5**–**7**) were purified by GC or Kugelrohr distillation and were characterized by NMR spectroscopy and either elemental analysis or exact mass determination. Adducts **2**–**4** were previously characterized.[9] In the cases of adducts **2**, **5**, **6**, and **7**, mixtures of syn and anti cyclopropanes were formed. Isomer identities were not assigned, but the isomer ratios were determined by capillary GC: **2**, 30:1; **5**, 5.2:1; **6**, 4:1; and **7**, 2.2:1.

The volatile side products that accompany the cyclopropanes include benzaldehyde, benzaldehyde dimethyl acetal, and methyl benzoate in very low (<5%) yields.[9] Nonvolatile products include azine ($(PhC(OMe){=}N{-})_2$) and the formal dimer of MeOCPh, both in less than 1% yield. Similar products are formed from **1** in pentane solution. Mechanisms involving the intermediacy of MeOCPh can be written to describe the origins of each of these products. For example, capture of MeOCPh by adventitious water (i.e., from imperfect drying of the diazirine preparation) leads to PhCH(OH)OMe and thence to benzaldehyde and methanol. Methanolic capture of MeOCPh leads to benzaldehyde dimethyl acetal. These suggestions are supported by appropriate experiments. Methyl benzoate (<1%) most likely represents capture of MeOCPh by oxygen.

Attempts to add MeOCPh to $Me_2C{=}CMe_2$, either thermally or photochemically, led only to the apparent rearrangement product, **8**, rather than to the anticipated cyclopropane.[9] It is possible that **8** is formed directly from MeOCPh and $Me_2C{=}CMe_2$ in an "ene"-type reaction. Experiments to test this possibility are in progress. Reactions of **1** with 6,6-dimethylfulvene[12] did not result in an isolable product.



8

Competition Reactions. Relative reactivities of MeOCPh toward the olefins were determined by the classical competition method.[13] Diazirine **1** was decomposed thermally at 25 °C in binary mixtures of at least 9-fold excesses of alkenes. The product cyclopropanes, which were stable under the decomposition conditions, were analyzed by capillary GC using a calibrated, flame-ionization detector and an electronic integrator.

The relative reactivity of olefin a vs. olefin b was calculated from eq 3, where P_i is the calibrated mole fraction of product cyclopropane and O_i is the initial mole fraction of an olefin.[13] The experimentally determined relative reactivities of MeOCPh appear in Table I.

$$(k_a/k_b) = (P_a/P_b)(O_b/O_a) \tag{3}$$

Reproducibilities are generally good; the highest uncertainly (±8%) is associated with the most reactive olefin, acrylonitrile

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(11) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(12) Moss, R. A.; Young, C. M.; Perez, L. A.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1981**, *103*, 2413.

(13) Review: Moss, R. A. In *Carbenes*; Jones, M., Jr.; Moss, R. A., Eds.; Wiley: New York, 1973; Vol. 1, p 153ff.

Table II. Relative Reactivities of MeOCPh and Other Carbenes[a]

alkene	MeOCPh[b]	MeCCl[c]	PhCCl[d]	PhCF[e]	CCl_2[f]	PhOCCl[g]	MeOCCl[h]	PhOCF[i]
$Me_2C{=}CMe_2$		7.44	25.5	33.2	78.4	3.0	12.6	7.14
$Me_2C{=}CHMe$	3.4	4.69	16.0	12.0				17.9
$Me_2C{=}CH_2$	10.6	1.92	5.0	6.67	4.89	7.3	5.43	14.3
trans-MeCH=CHMe	1.00	1.00	1.00	1.00	1.00	1.00[j]	1.00	
n-$C_4H_9CH{=}CH_2$	0.74					0.36		1.00
$CH_2{=}CHCOOMe$	172.	0.078	0.50	0.74	0.060	3.7	29.7	18.7
$CH_2{=}CHCN$	445.	0.074	0.55	0.80	0.047	5.5	54.6	33.6

[a] Data are at 25 °C except for CCl_2 (80 °C) and PhOCF (50 °C). All carbenes were generated from diazirines except CCl_2, which was produced by the thermolysis of $PhHgCCl_2Br$. [b] From Table I. [c] Data from ref 1c and 14. [d] Data from ref 15 and 16. [e] Data from ref 15 and 17. [f] Data from ref 1c. [g] Data from ref 18. [h] Data from ref 1b. [i] Data from ref 19. [j] The standard olefin in this case is *trans*-2-pentane.

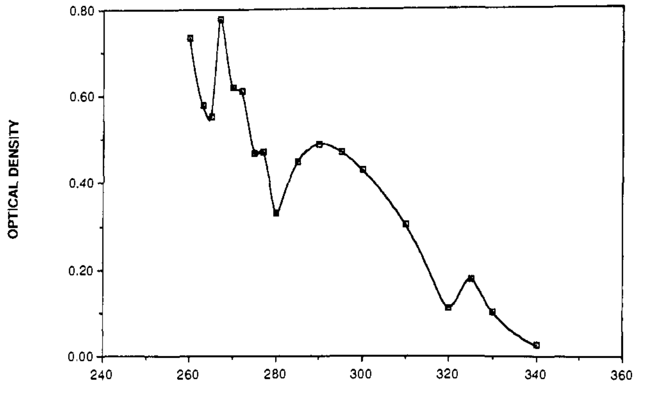


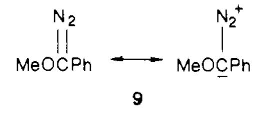
Figure 1. Point-by-point transient spectrum of MeOCPh determined by laser flash spectroscopy at 25 °C in pentane. The carbene has λ_{max} ~290 nm; the secondary maximum at ~325 nm is due to products. See text for discussion.

(case 4). Two cross-check[13] experiments were performed. From cases 4 and 5, we calculate $k_{rel}(CH_2{=}CHCOOMe/CH_2{=}CHCN) = 0.39$; the experimentally determined value is 0.48. From cases 1 and 5, we calculate $k_{rel}(CH_2{=}CHCOOMe/Me_2C{=}CHMe) = 51$. In this case, three experiments gave $k_{rel} = 73 \pm 2.5$. We have no explanation for the poor agreement, but the reactivity difference between these two substrates is certainly of this magnitude, as established by the absolute rate constant measurements described below.

For purposes of comparison, the experimental relative reactivities of MeOCPh from Table I have been normalized to a *trans*-butene standard and collected in Table II, where they are compared to existing data for other carbenes.[14-19] The set of alkenes in this table was selected to cover a broad range of carbenic philicity.[2] In contrast to our older set of nucleophilic alkylethylenes, the newer set also contains electron-deficient olefins that are particularly suited for reaction with ambiphilic or nucleophilic carbenes.

Finally, two additional studies require brief mention. Firstly, decomposition of **1** in *cis*-butene gave no **4**, corresponding to the *trans*-butene adduct of MeOCPh (capillary GC). This is consistent with stereospecific addition of MeOCPh to simple alkenes. Secondly, photolysis of **1** in the presence of cumene gave no benzene or toluene by capillary GC, seemingly excluding homolytic fragmentation in solution of MeOCPh to a methyl,phenyl radical pair and carbon monoxide.

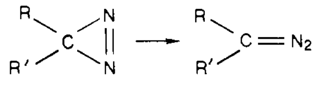
Diazoalkane Intermediacy. The extraordinary reactivity of MeOCPh toward acrylonitrile and methyl acrylate (Table II) demonstrates its ambiphilic or nucleophilic character (see below), but this exalted selectivity for electron-deficient alkenes could also signal the intervention of methoxyphenyldiazomethane, **9**, that



$$\overset{N_2}{\overset{\|}{MeOCPh}} \longleftrightarrow \overset{N_2^+}{\overset{|}{MeO\underset{-}{C}Ph}}$$

9

could form from **1** by isomerization. Diazoalkanes can rapidly add to electron-deficient olefins, forming pyrazolines that easily lose nitrogen to yield the same cyclopropanes expected from the corresponding carbene/alkene cycloadditions.[20] The isomerization of diazirines to diazoalkanes, eq 4, can occur either thermally or photochemically, and is particularly facile when R or R′ are electron-withdrawing substituents capable of stabilizing a negative charge on the diazo carbon atom (cf. **9**).[21] The reaction can also be reversible under certain conditions.[21]



(4)

10 **11**

Thus, when R,R′ are aryl, vinyl, alkyl, or trifluoromethyl, diazoalkanes intervene in the thermal decompositions of the diazirines.[22] However, as R,R′ become increasingly electron donating, the stability of **11** decreases, its detection becomes difficult, and its formation from **10** may be bypassed entirely in favor of a direct diazirine to carbene plus nitrogen pathway.[22] In eq 4, when R,R′ are Ph and Cl,[23] or Ph and Br,[24] traces of the diazo compound accompany the carbene as products of low temperature matrix UV irradiation of the diazirine. On the other hand, similar experiments where R,R′ = MeO[25] (or PhO[26]) and Cl, or MeO and F,[24] fail to show even traces of **11**; only the expected carbenes are produced. Thus, when both R and R′ feature lone-pair-carrying atoms bonded to the diazirine carbon atom, isomerization is eschewed.

What of diazirine **1**, where R,R′ = MeO,Ph? We examined the decompositions of **1**, and also of methoxymethyldiazirine, by laser flash photolysis in solution. Laser irradiation at 351 nm of **10** (R,R′ = MeO,Me)[27] in isooctane or acetonitrile solutions at 0–25 °C gave rise to weak UV absorption signals in the 370–430-nm region, appropriate to a diazo compound.[28] Point by point

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(14) Moss, R. A.; Mamantov, A. *J. Am. Chem. Soc.* **1970**, *92*, 6951.

(15) Moss, R. A.; Ławrynowicz, W.; Hadel, L. M.; Hacker, N. P.; Turro, N. J.; Gould, I. R.; Cha, Y. *Tetrahedron Lett.* **1986**, *27*, 4125.

(16) Moss, R. A.; Whittle, J. R.; Freidenreich, P. *J. Org. Chem.* **1969**, *34*, 2220.

(17) Moss, R. A.; Ławrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3828.

(18) Moss, R. A.; Perez, L. A.; Włostowska, J.; Guo, W.; Krogh-Jespersen, K. *J. Org. Chem.* **1982**, *47*, 4177.

(19) Moss, R. A.; Kmiecik-Ławrynowicz, G.; Krogh-Jespersen, K. *J. Org. Chem.* **1986**, *51*, 2168.

(20) For an example involving diphenyldiazomethane and for leading references, see: Tomioka, H.; Ohno, K.; Izawa, Y.; Moss, R. A.; Munjal, R. *Tetrahedron Lett.* **1984**, *24*, 5415.

(21) Heine, H. W. *Chem. Heterocycl. Compd.* **1982**, *42*, part 2, 595. Liu, M. T. H. *Chem. Soc. Rev.* **1982**, *11*, 127.

(22) Liu, M. T. H.; Tencer, M.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1986**, 211.

(23) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517. See also: Maltsev, A. K.; Zuev, P. S.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, *34*, 2159.

(24) Sheridan, R. S., private communication.

(25) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 99.

(26) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 844.

(27) Moss, R. A.; Fedorynski, M.; Kmiecik-Ławrynowicz, G.; Terpinski, J. *Tetrahedron Lett.* **1986**, *27*, 2707.

transient spectra exhibited maxima at 400 (in isooctane) or 390 nm (in CH_3CN). The decay of these signals, monitored at 400 nm, was characterized by $k \sim 3.7–11 \times 10^5$ s^{-1}, increasing with increasing concentration of the diazirine. The transient, most reasonably diazoalkane **11** (R,R′ = MeO,Me), could be quenched by acrylonitrile in acetonitrile, presumably by 1,3-dipolar addition. Analysis[4] of the lifetime of the transient vs. [acrylonitrile] gave $k_2 \sim 1.0 \pm 0.2_3 \times 10^6$ M^{-1} s^{-1} for the quenching reaction. Under the same reaction conditions, trimethylethylene did not quench the transient. These experiments offer evidence for the photoisomerization of methoxymethyldiazirine to methoxymethyldiazomethane, with rapid addition of the latter to the electron-deficient acrylonitrile but not to trimethylethylene.

In marked contrast, we found no evidence for photoisomerization of methoxyphenyldiazirine. No transient signal attributable to methoxyphenyldiazomethane could be seen in the 360–420-nm region upon laser flash photolysis of diazirine **1** at 351 nm. Instead, a strong transient absorption appeared at ~290 nm and was attributed to MeOCPh (see below). Tentatively, we conclude that the MeO,Ph combination of substituents leads to direct decomposition of photoexcited diazirine **1** to the carbene, MeOCPh. However, this does not prove that thermal decomposition of **1** (as in Table I) also bypasses the diazo compound. Direct determination of the absolute reaction rates of MeOCPh with alkenes therefore assumes great importance.

Absolute Rate Studies of MeOCPh. Our time-resolved flash spectroscopic studies employed equipment and techniques similar to those previously described.[4] The laser light source was a Lambda Physik EMG 101 excimer laser, operating at 351 nm and emitting 14-ns light pulses at ~90 mJ. The detection unit consisted of a 1000-W Oriel xenon arc lamp, a 1-in. Uniblitz shutter, grating monochromator, and a RCA 4840 photomultiplier tube wired in a five-dynode configuration. A block diagram of the system can be obtained upon request. The transient data were acquired by a Tektronix 7912 AD transient digitizer and analyzed by a Tektronix 4052A computer. The digitizer was capable of generating a 512 point trace with a minimum resolution of 500 ps/point.

Laser flash photolysis at 351 nm and 25 °C of freshly prepared pentane solutions of diazirine **1** in 1- × 1-cm Suprasil quartz cells gave a mixture of benzaldehyde, methyl benzoate, and benzaldehyde dimethylacetal, similar by capillary GC to that obtained from the steady-state, broad band photolysis (see above). The pulsed laser irradiation gave rise to a strong transient absorption signal within the time period of the laser pulse. Analysis of this signal as a function of wavelength allowed construction of the point-by-point spectrum shown in Figure 1. We assign the maximum at 290 nm to MeOCPh. At 77 K in a 3-methylpentane glass, the carrier of the 290-nm signal is long-lived, but it decays at ambient temperature on the microsecond time scale, with $\tau \sim 15–30$ μs and $k \sim 1–2 \times 10^4$ s^{-1}. Additionally, the MeOCPh absorption can be quenched with acrylonitrile, methyl acrylate, methanol, or *tert*-butyl alcohol (see below).

The secondary maximum at ~325 nm in Figure 1 is probably due to products derived from MeOCPh, such as benzaldehyde and methyl benzoate, that have absorption maxima in this region. Indeed, the 325-nm signal grows in with time and accumulates with repeated laser pulses. Its buildup prevents the 290-nm carbene transient absorption from returning to the original base line and makes it necessary to perform all laser kinetic experiments on virgin diazirine solutions. On occasion, strong contributions of the 325-nm absorption prevented observation of decay at 290 nm.

In the presence of a sufficient concentration of a reactive quencher, the kinetics of the interception of MeOCPh could be followed by monitoring the disappearance of its absorption at 290 nm. It was necessary to operate on a short instrumental time scale (≤1 μs) to avoid complications due to product absorptions (see above).

The decay of PhCCl, for example, follows eq 5, where k_{obsd} is the observed pseudo-first-order rate constant for carbene decay, k_o is the corresponding rate constant in the absence of quencher, and k_2 is the second-order rate constant for the quenching reaction.[4]

$$k_{obsd} = k_o + k_2[\text{quencher}] \qquad (5)$$

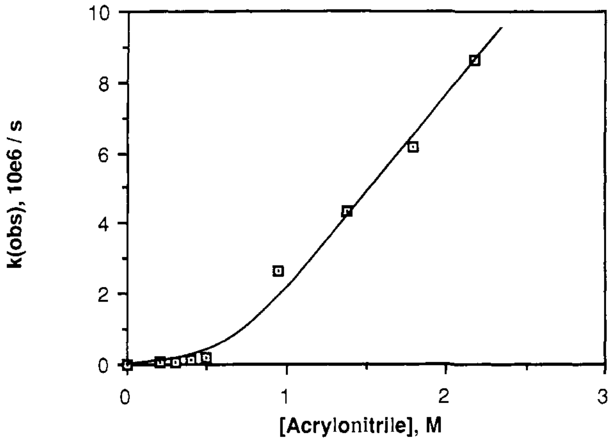

Figure 2. Observed pseudo-first-order rate constants for decay of MeOCPh at 290 nm vs. [acrylonitrile], M, in pentane at 25 °C. See text for discussion.

Table III. Apparent Rate Constants for MeOCPh Addition Reactions

olefin	k_2, M^{-1} s^{-1} [a]	k_2^{rel}(laser) [b]	k_2^{rel}(comp) [c]
$CH_2{=}CHCN$	$5.4 \pm 0.9_3 \times 10^6$	3.2	2.6
$CH_2{=}CHCOOMe$	$1.7 \pm 0.2_2 \times 10^6$ [d]	1.0	1.0

[a] Errors are average deviations of *n* (subscript) runs. See text for discussion. [b] Ratio of the apparent absolute rate constants (k_2). [c] From cases 4 and 5 of Table I. [d] Plots of k_{obsd} vs. [$CH_2{=}CHCOOMe$] exhibited concave upward curvature at lower concentrations of quencher. The second-order rate constants are derived from portions of the plots where the quencher concentrations are varied between 1.2 and 2.8 M in pentane. See text for a discussion of curvature in these plots.

The kinetics of MeOCPh decay follows a more complicated scheme. Both methyl acrylate and acrylonitrile quench the carbene, and capillary GC demonstrates the presence of cyclopropanes **6** or **7** in the laser photolysates. However, in pentane at 25 °C, there is curvature in the correlation of the observed rate constant for carbene decay vs. the concentration of (either) quencher.

Figure 2 illustrates this behavior with acrylonitrile. Above ~0.5 M acrylonitrile the correlation becomes linear with slope $\sim 4.9 \times 10^6$ M^{-1} s^{-1}. However, doubling [acrylonitrile] from 1.0 to 2.0 M increases k_{obsd} by >3, so that the apparent kinetic order in quencher exceeds unity and is not in accord with eq 5. Similar behavior is observed with methyl acrylate.

One possible explanation of this behavior focuses on the pronounced nucleophilicity of MeOCPh and recognizes that additions to methyl acrylate or acrylonitrile would be "Michael-like", traversing dipolar transition states where marked kinetic solvent polarity effects could be expected. Thus k_{obsd} would increase as the concentration of (polar) quencher in pentane increased. On the other hand, the *relative* rate constant for the competition between acrylonitrile and isobutene (in pentane) is reasonably constant at ~40 over the concentration range 0.25–1.5 M in acrylonitrile. One would expect the addition to the nitrile to proceed via a more polar transition state than the addition to isobutene, so that k_{rel} might be expected to increase with increasing solvent polarity (increasing [acrylonitrile]). We are continuing our study of solvent effects in MeOCPh chemistry.

For the present discussion, we will take the apparent dependence of k_{abs} on [quencher] as a measure of MeOCPh reactivity toward these olefins, restricting ourselves to the linear portions of the correlations. The slopes (apparent rate constants) thus obtained appear in Table III.

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(28) A description of the laser flash photolysis system appears below.

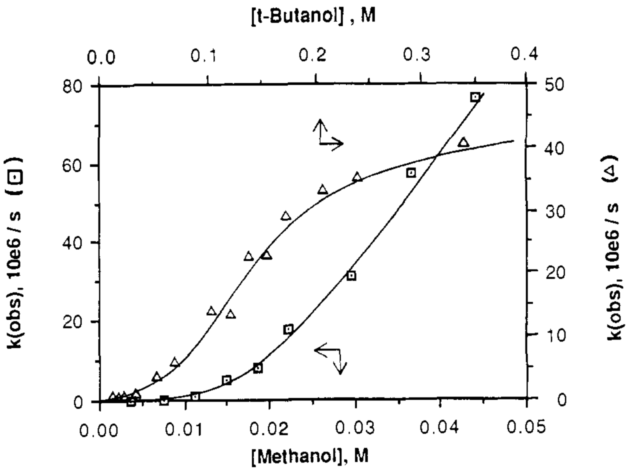


Figure 3. Quenching of MeOCPh by alcohols at 298 K; methanol (□, bottom and left scales) and *tert*-butyl alcohol (Δ, top and right scales) in pentane. The continuous trace is an arbitrary fit to the data.

Relative rates for MeOPh additions to CH_2=CHCN vs. CH_2=CHCOOMe can be determined either from the ratio of absolute rate constants (for which we use the apparent rate constants in Table III) or by the classical, product-based competition method (Table I). A comparison of the results obtained by the two methods also appears in Table III and demonstrates reasonable agreement.

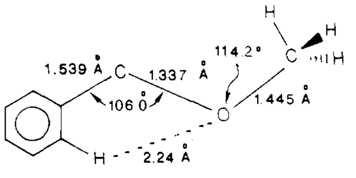
A more important comparison is the reactivity of acrylonitrile vs. trimethylethylene. Significant intervention of diazo compound **11** (R,R′ = MeO,Ph) in either the photochemical or thermal decompositions of diazirine **1** might augment the cyclopropane product stemming from the electron-deficient acrylonitrile (by 1,3-dipolar addition of the diazo compound) at the expense of the product from trimethylethylene (which should be formed only from the carbene). Is the large relative reactivity for CH_2=CHCN/Me_2C=CHMe (~130 as calculated from Table I) indicative of diazo compound intermediacy?

Taking 130 as the true relative rate constant for the competitive addition of MeOCPh to CH_2=CHCN and Me_2C=CHMe, we can estimate that k_2 for the addition of the carbene to trimethylethylene is $\sim 5.4 \times 10^6/130 \sim 4.2 \times 10^4$ M^{-1} s^{-1}. In 1 M trimethylethylene/pentane, the pseudo-first-order rate constant for decay of MeOCPh would therefore be $\sim 4 \times 10^4$ s^{-1}, about equal to the rate constant for decay of MeOCPh in pentane solution alone (see above). Indeed, trimethylethylene fails to quench the 290-nm absorption of MeOCPh, even in pure alkene. Thus, as we estimated, the addition of MeOCPh to trimethylethylene is much slower than its addition to acrylonitrile, so that the large, product-based k_{rel} of Table I is appropriate to the carbene. Although this does not completely exclude the intervention of **11** in thermal decomposition of **1**, it strongly suggests that the competitive rate constants are not seriously biased by diazoalkane reactions.

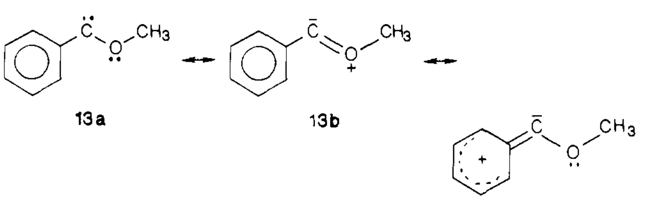
We also observed that MeOCPh could be quenched by methanol or *tert*-butyl alcohol in pentane solution. The kinetic behavior as a function of [alcohol] was similar to that reported for the corresponding reactions of arylchlorocarbenes, including concave-upward or concave-downward dependencies of k_2^{obsd} on [ROH] for methanol or *tert*-butyl alcohol, respectively.[29] These curves appear in Figure 3. Using the mathematical treatment of Griller et al.,[29] we find that the reaction of MeOCPh with oligomeric methanol in pentane is diffusion controlled ($k > 1 \times 10^{10}$ M^{-1} s^{-1}), whereas the carbene's reaction with monomeric *tert*-butyl alcohol in pentane has $k_2 \sim 2.7 \times 10^8$ M^{-1} s^{-1}, about 100 times greater than the comparable rate constant for *p*-anisylchlorocarbene.[29]

Calculations. In order to provide further characterization of MeOCPh, and to deepen comparison with the properties of other carbenes,[18,19] we carried out a series of molecular orbital calculations. We determined the geometries and relative energies of several low-energy conformers of MeOCPh, prompted by reports that ClCOMe[25] and ClCOPh[26] exist in two configurationally stable isomeric forms (presumably cis and trans) at cryogenic temperatures. Our calculations also provide the energies of the frontier molecular orbitals of MeOCPh, essential to further clarification of the carbene's philicity.

The calculations are of the ab initio restricted Hartree–Fock type and use the standard basis sets and methods available in the GAUSSIAN 82 series of programs.[30] A DEC Vax 11/780 computer was employed throughout. Five geometrical parameters were considered important and therefore optimized by using the minimal STO-3G basis set for each conformation of MeOCPh: the C–C(Ph), C–O, and O–C(Me) bond lengths, as well as the C-(Ph)–C–O and C–O–C(Me) bond angles. The internal structures of the phenyl and methyl groups were fixed with standard bond lengths and angles [C–C = 1.40 and C–H = 1.08 Å in Ph, C–H = 1.09 Å in Me, and all bond angles at 120° for Ph or 109.47° for Me].[31] Improved energies were then obtained through single point calculations at these partially optimized geometries, by using the split valence 4-31G basis set.[30] Population analysis of the wave functions employed the conventional partitioning techniques due to Mulliken.[32] The entire computational procedure is fully compatible with previous work by us and others on related carbenes.[3,18,19] In accord with our expectations, the most stable conformer of MeOCPh is calculated to be the trans species, **12**, where the phenyl group is coplanar with the C–O–C(Me) fragment and one of the methyl hydrogens eclipses the carbenic lone pair. This minimum is characterized by a typical singlet carbene bond angle of 106°, and a substantial dissimilarity of more than 0.1 Å between the (carbenic)C–O and O–C(Me) bond lengths. The latter bond length of 1.445 Å is in the normal range for C–O single bonds (1.44–1.47 Å), whereas the short (carbenic)C–O bond (1.337 Å) is indicative of substantial double bond character arising from π-donation from O to the formally empty carbon 2p(π) orbital; cf. structures **13a** ↔ **13b**. In fact, the population analysis shows that only 1.77 electrons reside in the formally doubly occupied oxygen 2p(π) orbital, whereas the C 2p(π) orbital is populated by 0.28 electrons. The calculated contraction of this C–O bond is in accord with previous results on (e.g.) FCOPh[19] and HCOH.[33]



12 (*trans*-MeOCPh)



13a **13b** **13c**

The C–C(Ph) single bond in **12** is not particularly short, indicating that the double bond character in this bond is low and that phenyl π-donation to the carbenic center is minimal. In **13**, therefore, the contribution of **13c** is small compared to that of **13b**. The population analysis shows that the entire phenyl π-system is deficient by only 0.08 electrons, so that the oxygen

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[29] Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

[30] Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fludes, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, Release H, Carnegie-Mellon University, Pittsburgh, PA, 1984.

[31] Pople, J. A.; Gordon, M. *J. Am. Chem. Soc.* **1967**, *89*, 4253.

[32] Mulliken, R. S. *J. Chem. Phys.* **1955**, *22*, 1833, 1841, 2338, 2343.

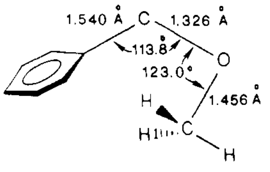
[33] Goddard, J. D.; Schaeffer, H. F., III. *J. Chem. Phys.* **1979**, *70*, 5117.

π-donation is about 2.5 times larger (0.20 e vs. 0.08 e) than that of phenyl.

We find that there is free rotation of the methyl group in the trans conformer of PhCOMe, because the energy of the conformer where the methyl hydrogens are staggered relative to the carbene lone pair is only 0.7 kcal/mol higher than that of **12**. No significant structural changes accompany rotation of the methyl group. In contrast, somewhat restricted rotation is predicted for the phenyl group. The conformer where the phenyl group is perpendicular to the (Ph)C–C–O–C(Me) plane is 8.2 kcal/mol higher in energy than **12**, a surprisingly large value considering the modest π-donation from phenyl. The population in the carbenic 2p(π) orbital actually decreases by only 0.03 e in the perpendicular conformer, relative to **12**. Moreover, the C–C(Ph) bond length increases by only 0.008 Å during phenyl rotation, and only minor geometrical changes occur in the remainder of the molecule. This supports the contention that there is very little C–C(Ph) double bond character (**13c**) present in **12**.

Examination of the interatomic distances provides a clue to the origin of the large rotational phenyl barrier in **12**. An ortho hydrogen atom of the phenyl group is only 2.24 Å away from the oxygen atom, and intramolecular hydrogen bonding with the in-plane oxygen lone pair may be an additional stabilizing factor in planar (but not perpendicular) *trans*-MeOCPh.

A secondary minimum for MeOCPh is represented by the cis conformer, **14**, where, for steric reasons, the phenyl group is necessarily perpendicular to the (Me)C–O–C plane. In **14**, significant openings of 8–9° are calculated for the (Ph)C–C–O and C–O–C(Me) bond angles relative to **12**. These expansions reduce the steric interactions and make it possible for the bond lengths in **14** to be very similar to those in **12**. Most importantly, the (carbenic)C–O double bond character is preserved in **14**. Rotation of the phenyl group is impossible for steric reasons, but the barrier to methyl group rotation remains small at 0.4 kcal/mol; geometrical changes upon methyl group rotation are minimal.



14 (*cis*-MeOCPh)

The cis conformer, **14**, is calculated to lie 14.3 kcal/mol above the trans conformer, **12**. The cis–trans energy difference for the MeOCPh conformers is thus considerably larger than that calculated previously for FCOPh (3.8 kcal/mol)[19] or HCOH (5–7 kcal/mol).[33] This increase further exemplifies the energetic cost of the steric bulk associated with having the phenyl group directly linked to the carbenic center (viz., the increases in bond angles and the loss of the postulated H-bonding in **14** relative to **12**). In contrast, cis–trans isomerization in FCOPh or HCOH is accompanied by only minor skeletal changes.[19,33]

We also modeled the structure of the transition state for MeOCPh cis–trans interconversion ($\mathbf{12} \rightleftharpoons \mathbf{14}$). We fixed the (Ph)C–C–O–C(Me) dihedral angle at 90° and kept the phenyl group coplanar as in **12**. The energy of this conformation is 25.0 kcal/mol above **12** or 10.7 kcal/mol above **14**. The increased energy arises from the nearly complete destruction of the stabilizing partial (carbenic)C–O double bond of **12** or **14** in the perpendicular transition state orientation; this is reflected by substantial lengthening of the bond to 1.408 Å. The 25 kcal/mol barrier to trans → cis isomerization of MeOCPh (i.e., conversion of **12** to **14**) is similar to that calculated for the analogous isomerization of HCOH (27.5 kcal/mol)[33] and larger than that for FCOPh (17 kcal/mol).[19]

Finally, the relevent quantities for a frontier molecular orbital (FMO) analysis of carbenic philicity are the orbital energies associated with the carbene's HOMO (σ-type lone pair) and LUMO (2p(π) vacant orbital), both on the carbenic C atom.[2] The appropriate calculated energies appear in Table IV for MeOCPh conformers **12** and **14**.

Table IV. Calculatd Frontier Molecular Orbital Energies (eV) for MeOCPh[a]

orbital	*trans*-MeOCPh (**12**)	*cis*-MeOCPh (**14**)
LUMO (p)	2.39	3.52
HOMO (σ)[b]	−9.38	−8.38

[a] Energies are calculated at the 4-31G basis set level for STO-3G partially optimized geometries; see text. [b] There are two phenyl group π orbitals energetically higher than the carbenic σ orbital, but these are not relevant to the FMO analysis.

Both the HOMO and LUMO of *cis*-**14** are of higher energy than the corresponding orbitals of *trans*-**12** (with potentially important chemical consequences; see below). The destabilization of the HOMO by 1.0 eV is primarily due to the larger angle at the carbenic center in **14**, which reduces the 2s character in the lone pair (HOMO) orbital. The raising of the LUMO appears to be associated with the absence of interaction between the unoccupied phenyl (π^*) and the carbenic (2p) orbitals in **14**. Thus the LUMO of **14** is more like a pure C 2p(π) orbital than the LUMO of **12**, where there is substantial phenyl (π^*) mixing.

A referee questioned whether the inclusion of correlation energy corrections would alter the HOMO and LUMO energies calculated for **12**, **14**, and the transition state connecting them. It is likely that minor alterations would occur, but due to the considerable molecular size of **12** such calculations are unfortunately impossible to carry out with the current technology. However, Goddard and Schaefer found in their calculational study of hydroxycarbene that correlation energy corrections had only minor effects on the relative energetics.[33] Thus, the relative energy of *trans*- vs. *cis*-hydroxycarbene was reduced by 3 kcal/mol, relative to the Hartree–Fock value, and the transition state energy was increased by a similar amount. Relative energy changes of this magnitude (~3 kcal/mol) would not substantially alter any of our conclusions drawn on thermodynamic grounds.

Discussion

The data in Table II leave no doubt that MeOCPh is an ambiphilic carbene:[1,2] it behaves as an electrophile toward electron-rich alkenes (viz. isobutene > *trans*-butene > 1-hexene)[34] but as a nucleophile toward electron-poor alkenes (acrylonitrile > methyl acrylate > 1-hexene). MeOCPh thus joins the other known ambiphiles, MeOCCl,[1b] PhOCCl,[18] and PhOCF,[19] all of which are also oxacarbenes. The selectivity of MeOCPh toward the electron-deficient olefins is extraordinary, even for an ambiphile (Table II), and, of course, dramatically different from the suppressed selectivity of the electrophiles MeCCl, PhCCl, PhCF, or CCl_2 toward these substrates.

Application of FMO theory[2,3] to the MeOCPh/alkene cycloadditions leads to a satisfactory rationalization of these experimental trends. Using the admittedly arbitrary[18] procedure of combining calculated carbene and experimental olefin FMO energies, we take the calculated HOMO (σ) and LUMO (p) energies of either *trans*-MeOCPh or *cis*-MeOCPh (Table IV), together with the experimental HOMO (π) and LUMO (π^*) energies for the alkenes, to derive the differential orbital energies ($\mathrm{LUMO_{carbene}}-\mathrm{HOMO_{alkene}}$) and ($\mathrm{LUMO_{alkene}}-\mathrm{HOMO_{carbene}}$). The former term (p–$\pi$) represents *electrophilic* interaction of the vacant carbenic p orbital with the alkene π^* orbital, whereas the latter term (π^*–σ) measures *nucleophilic* interaction of the filled carbenic σ orbital with the empty alkene π^* orbital. The differential orbital energies appear in Table V.

If we assume substantial (nearly equal) p–π and σ–π^* carbene/alkene orbital *overlap*[2,3] in the cycloaddition transition state, then we can relate the calculated differential orbital energies to carbenic philicity. If ($\mathrm{LUMO_{carbene}}-\mathrm{HOMO_{alkene}}$) < ($\mathrm{LUMO_{alkene}}-\mathrm{HOMO_{carbene}}$) over the entire set of substrate al-

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(34) We attribute the isobutene > trimethylethylene inversion to the operation of a steric effect. Related steric effects have been observed in the reactions of PhOCCl[18] and PhOCF[19] with tetramethylethylene.

(35) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341. Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.

Table V. Differential Orbital Energies (eV) for MeOCPh/Alkene Additions[a]

alkene	*trans*-MeOCPh (**12**) p–π	*trans*-MeOCPh (**12**) π^*–σ	*cis*-MeOCPh (**14**) p–π	*cis*-MeOCPh (**14**) π^*–σ
$Me_2C=CMe_2$	10.66	11.65	11.79	10.65
$Me_2C=CHMe$	11.07	11.62	12.20	10.62
$Me_2C=CH_2$	11.63	11.57	12.76	10.57
trans-MeCH=CHMe	11.51	11.48	12.64	10.48
$CH_2=CH$-*n*-C_4H_9[b]	11.91	11.37	13.04	10.37
$CH_2=CHCOOMe$	13.11	10.18	14.24	9.18
$CH_2=CHCN$	13.31	9.59	14.44	8.59

[a] For alkene π^* and π orbital energies, see ref 2 and 35. Carbene orbital energies are from Table IV. [b] ϵ_π^* is approximated with the value for propene; ϵ_π is approximated with the value for 1-pentene.[35]

kenes, the carbene is electrophilic toward these substrates. On the other hand, an inverted inequality of the differential orbital energies signifies a nucleophilic carbene. Finally, a *crossing* of the differential orbital energies, in the midst of the substrate set, is consistent with ambiphilic reactivity.

In accord with this scheme, the experimentally observed ambiphilic reactivity of MeOCPh (Table II) parallels the expected ambiphilicity of *trans*-MeOCPh (**12**), as implied by the differential orbital energies of Table V. Note, however, that the crossover between the (p–π) and (π^*–σ) energies occurs "early" in the substrate set, with (p–π) ~ (π^*–σ) for both isobutene and *trans*-butene, suggesting that the nucleophilic properties of MeOCPh should be very pronounced.

Indeed, the relative reactivities of MeOCPh toward methyl acrylate and acrylonitrile are greater than those of the other ambiphilic carbenes in Table II. This finding is implicit in Table V, where the differential orbital energy characteristic of nucleophilic interaction, π^*–σ, is relatively small (9.59 eV) for (e.g.) the addition of *trans*-MeOCPh to acrylonitrile (and even smaller at 8.59 eV for *cis*-MeOCPh). In fact, the calculated (π^*–σ) energy is lower for this reaction of *trans*-MeOCPh than it is for the comparable reactions of the other ambiphiles: PhOCCl (10.99),[18,36] PhOCF (12.02),[19] or MeOCCl (11.03).[2,37]

The magnitudes of the differential orbital energies are related in an inverse sense to their contributions to the stabilization energy of the reaction transition state and therefore in a direct sense to the activation energy of the reaction.[3] We expect that, as the π^*–σ energy decreases for the addition of a nucleophilic carbene, the activation energy will decrease and the rate will increase. The prediction, then, is for high nucleophilic reactivity of MeOCPh toward the electron-deficient alkenes, as is indeed observed. However, we must point out that the high relative reactivity of MeOCPh toward acrylonitrile does not seem to be paralleled by a high absolute reactivity. The apparent k_2 value for this reaction (5.4×10^6 M^{-1} s^{-1}) is not particularly high: FCPh reacts with acrylonitrile with $k_2 = 1.2 \times 10^6$ M^{-1} s^{-1} [15] only 4.5 times more slowly, even though (π^*–σ) for this reaction is ~10.44 eV, about 0.85 eV higher than that for *trans*-MeOCPh and acrylonitrile. Of course, π^*/σ overlap will be reduced in the addition of FCPh to acrylonitrile, relative to the comparable MeOCPh reaction, mitigating the disparities in differential orbital energies.

Note, also, from Table V that *cis*-MeOCPh (**14**) is predicted to be a *nucleophile* toward all alkenes in the substrate set. Both its HOMO and LUMO energies are higher than those of *trans*-MeOCPh (Table IV), and these changes favor increased nucleophilicity in the additions of **14**, relative to those of **12**. However, the overall energy of **14** is calculated to be 14 kcal/mol above that of **12**, with a barrier of only ~11 kcal/mol to cis → trans interconversion. It may therefore be unlikely that the sterically less hindered cis carbene (**14**) participates in the slower cycloadditions to the alkylethylenes. Indeed, the large stereoselectivity (30:1) and low overall reactivity (Table II and absolute rate studies) in the trimethylethylene–MeOCPh reaction suggest that here the carbene reacts in its more hindered trans form.[34]

Table VI. Carbenic Philicity of Selected Carbenes

carbene[a]	$m_{CXY}{}^{calcd\,b}$	ϵ(HOMO)[c]	ϵ(LUMO)[c]	obsd philicity[d]
ClCMe	0.58	−10.28	1.61	E
BrCPh	0.64	*e*	*e*	E
ClCPh	0.71	*e*	*e*	E
CBr_2	0.82	*e*	*e*	E
FCPh	0.96	−10.23	1.51	E
CCl_2	1.00	−11.44	0.31	E
FCCl	1.22	−11.98	1.03	E
MeOCPh	1.34	−9.38	2.39	A
CF_2	1.47	−13.38	1.89	E
PhOCCl	1.49	−10.78	2.02	A
MeOCCl	1.59	−10.82	2.46	A
PhOCF	1.74	−11.81	2.56	A
MeOCF	1.85	−11.81	3.19	*f*
$(MeO)_2C$	2.22	−10.81	4.09	N[g]

[a] The oxacarbenes are considered only in their trans configurations; see text. [b] Calculated from eq 6. [c] Orbital energies are calculated in eV at the 4-31G level; see ref 3, 18, and 19 and text. [d] Philicity based on experiments: E = electrophilic, A = ambiphilic, N = nucleophilic. [e] Not available. [f] Not determined. [g] See the discussion and citations in ref 42.

However, *cis*-MeOCPh might be involved in the faster cycloadditions (e.g., to acrylonitrile). That is, with a preexponential factor of ~10^{13}–10^{14} s^{-1}, and an activation energy of 10.7 kcal/mol, we can estimate $k \sim 1.4 \times 10^5$ to 1.4×10^6 s^{-1} for the **14** → **12** isomerization at 25 °C. Thus, if the decomposition of diazirine **1** gives rise to *some* MeOCPh "born" in the cis form, then addition to acrylonitrile ($k_{obsd} \sim 5.4 \times 10^6$ M^{-1} s^{-1}, Table III) could occur prior to isomerization.

It is perhaps surprising to realize that, with a given alkene substrate, differential orbital energies alone predict an even greater nucleophilic (π^*–σ) component in the addition of *trans*-MeOCPh than in that of the archetypal nucleophilic carbene *trans*-$(MeO)_2C$. This is a result of the higher lying, accessible HOMO of MeOCPh, −9.38 vs. −10.81 eV for $(MeO)_2C$.[3] Indeed, as is shown in Table VI, MeOCPh has an unusually high HF/4-31G level calculated HOMO compared to most other oxa- or halo-substituted carbenes,[2,3,18,19] so that strongly pronounced nucleophilic properties should be anticipated. For comparison, we also calculated the HOMO and LUMO energies of (trans) MeOCH and MeOCMe. These are as follows (HO and LU, in eV): MeOCH, −9.73, 3.47; MeOCMe, −9.37, 3.81. These carbenes have HOMO energies comparable to that of MeOCPh, and LUMO energies that are significantly higher, so that they should also exhibit marked nucleophilic behavior.

We caution, however, that philicity depends not only on differential orbital energies but also on the comparative extents of p/π and σ/π^* orbital overlaps in the cycloaddition transition state. The very stable[3] $(MeO)_2C$ would be expected to add via a "late" transition state, where σ/π^* overlap is very well developed.[3] This could enhance the nucleophilic character of its addition reactions relative to those of MeOCPh, presumably a less stabilized carbene, that would transit an earlier transition state with inferior σ/π^* overlap.

It remains to consider the discrepancy between the experimentally observed, FMO-rationalized ambiphilicity of MeOCPh and the electrophilicity anticipated on the basis of empirical extrapolations.[2] Some time ago, we developed a correlation of carbenic selectivity based on linear free energy relations.[1a,2] The key parameter was m_{CXY}, the "carbenic selectivity index", defined as the least-squares slope of the correlation between (the logs of) the relative reactivities of CXY vs. those of CCl_2 in additions to a standard set of alkenes. Experimental m_{CXY} values for nine carbenes could be correlated by eq 6, where $\sum_{X,Y}$ represents the sum of the appropriate substituent constants for X and Y and m_{CCl_2} is set equal to unity.[1a,2]

$$m_{CXY} = -1.10\sum_{X,Y}\sigma^+_R + 0.53\sum_{X,Y}\sigma_I - 0.31 \qquad (6)$$

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[36] Perez, L. A. Ph.D. Dissertation, Rutgers University, New Brunswick, NJ, 1984, p 40.

[37] A similar situation holds for the π^*–σ values for additions of these ambiphiles to methyl acrylate.

Equation 6 permits the calculation of m_{CXY} for any carbene as long as the substituent parameters are available. In Table VI, we have arranged 14 carbenes in order of increasing m_{CXY}^{calcd}, as derived from eq 6. Excepting MeOCPh, the carbenes ClCMe through CF_2 have generally been found to react as electrophiles toward the common olefins.[2] ClCMe,[1c] ClCPh,[15] FCPh,[15] CCl_2,[1c] and CF_2,[38] for example, are demonstrably electrophilic toward either the alkenes of Table II or a series of appropriately substituted styrenes. On the other hand, PhOCCl,[18,39] MeOCCl,[1b,40] and PhOCF[19] are experimentally ambiphilic toward these substrates. MeOCF, though not yet characterized, is anticipated to be ambiphilic,[2,41] whereas $(MeO)_2C$ behaves as a nucleophile.[2,42]

Considerations such as these led us to define a "carbene selectivity spectrum."[1c,2] Carbenes with $m_{CXY}^{calcd} \leq 1.47$ were considered to be in the electrophilic region, those with $1.48 < m_{CXY}^{calcd} < 2.2$ were located in the ambiphilic zone, and carbenes with $m_{CXY}^{calcd} \geq 2.2$ were classed as nucleophiles (e.g., $(MeO)_2C$ or $MeOCNMe_2$, $m_{CXY}^{calcd} = 2.91$[2,3,43]). This classification scheme stimulated several investigations in the realm of ambiphiles. One outcome was the apparent definition of a "border" between electrophilic carbenes, represented by CF_2 ($m_{CXY}^{calcd} = 1.47$), and ambiphilic carbenes, represented by PhOCCl ($m_{CXY}^{calcd} = 1.49$);[18] c.f. Table VI.

The present study, however, shows that this border is incorrect; MeOCPh ($m_{CXY}^{calcd} = 1.34$) is found to be ambiphilic, and MeOCMe[27] ($m_{CXY}^{calcd} = 1.21$) may also be an ambiphile,[44] although its chemistry is complicated by the probable intervention of a diazoalkane (see above). In any event, ambiphilicity must extend into the previously defined "electrophilic" region of the carbene selectivity spectrum.

Reference to the orbital energies in Table VI suggests an explanation. With a given olefinic substrate or set of substrates, and assuming relatively constant orbital overlaps, the electrophilic properties of CXY will be developed by lowering its LUMO (p), so as to decrease the carbene p–olefin π differential orbital energy. The nucleophilic properties of CXY will be developed by raising its HOMO (σ) orbital, thus decreasing the olefin π^*–carbene σ energy. Conversely, raising the carbene's p orbital energy, or lowering its σ orbital energy, will produce the opposite effects of increasing the p/π or π^*/σ gaps, respectively, thus suppressing the electrophilic or nucleophilic properties of CXY.

From Table VI, we can see that CF_2 has the lowest HOMO energy (−13.38 eV), due to stabilization by the pair of electronegative F atoms, ensuring that the nucleophilic properties of CF_2 are minimized. On the other hand, the HOMO of MeOCPh is the highest, thus bringing its nucleophilic properties to the fore. Disregarding overlap for the moment, we can see that the expressed electrophilicity of CCl_2 certainly owes something to its very low LUMO energy. Its neighbor carbene, CFCl, will probably remain in the electrophilic camp when it is tested against $CH_2{=}CHCN$ or $CH_2{=}CHCOOMe$, both because of its low LUMO and very low HOMO energies. Moreover, the nucleophilicity of $(MeO)_2C$ is due not only to a relatively high-lying HOMO (those of ambiphilic MeOCCl or PhOCCl are comparable) but also to its very high LUMO energy that discourages electrophilic reaction.

Of course, the increase in π^*/σ overlap, and corresponding decrease in p/π overlap,[3] encountered as we travel down the array of carbenes in Table VI will strongly influence the specific balance of electrophilic and nucleophilic properties of a given carbene. Nevertheless, the calculated energies of the carbene's frontier orbitals give a quick "read" on what kind of reactivity to expect.

Experimental Section

General Methods. Proton NMR spectra were determined on Varian T-60 or XL-400 spectrometers. Preparative GC used Varian Models 90-P or 1700 instruments (injectors, 210 °C; detectors 280 °C). Capillary GC employed a Varian Model 3700 flame-ionization instrument. Mass spectra were determined with a VG 7070 (United Kingdom) mass spectrometer. Microanalyses were performed by Robertson Laboratory, Florham Park, NJ.

3-Methoxy-3-phenyldiazirine (1). A solution of 1.0 g (5.1 mmol) of 3-bromo-3-phenyldiazirine[10,11] (purified by short-column chromatography with silica gel and pentane) was prepared in 5 mL of distilled dimethylformamide (DMF). This was added to a mechanically stirred suspension of 1.5 g (27.8 mmol) of fresh sodium methoxide (Aldrich) in 30 mL of DMF at −12 °C. All operations were conducted under an atmosphere of dry nitrogen. The progress of the exchange reaction (eq 1) was monitored by TLC on Baker precoated silica gel on polyester sheets, where, with hexane eluent, product **1** had $\sim R_f$ 0.1, whereas the starting material had R_f 0.4.

After completion of the exchange reaction, the reaction mixture was cooled to −30 to −40 °C and 150 mL of brine (at 0 °C) was added. The cold reaction mixture was then extracted with 3 × 20 mL of spectrograde pentane. (The pentane and extraction equipment were precooled to 0 °C.) The combined pentane extract was dried over $CaCl_2$ and then concentrated to ~5 mL under vacuum at −20 °C. This solution was rapidly passed through a short silica gel column (jacketed at 0 °C) under nitrogen pressure to give a yellow-green solution of diazirine **1** in pentane in ~50% yield. IR, UV, and NMR spectra of 1 have been described above and in ref 9. It is important to keep solutions of 1 dry; the carbene reacts with water.

Synthesis of Cyclopropanes. General Procedure. A 10-fold molar excess of the desired alkene was mixed with the pentane solution of diazirine **1** (~1.5 mmol of **1**) in a Pyrex, screw-top Carius tube. The tube also contained a magnetic stirring bar. The reaction solution was stirred and either (a) irradiated with a 275-W G.E. Sunlamp at −10 °C for 2 h, (b) decomposed thermally (dark) with stirring at 45 °C for 30 min, or (c) decomposed thermally at 25 °C for 90 min. All three procedures gave comparable results. The reactions were considered complete upon bleaching of the yellow-green color of **1** and the cessation of N_2 evolution. After the removal of volatile solvents and alkenes, the crude adducts **2**–**7** were purified by Kugelrohr distillation or preparative GC on a 7-ft × 0.25-in. 10% SE-30 on Anakrom ABS column. Analytical GC employed a 12-m × 0.22-mm SE-30 bonded-phase vitreous silica capillary column and flame-ionization detection. The N_2 carrier gas flow rate was 25 mL/min, and the column was held at 130 °C.

1-Methoxy-1-phenyl-2,2,3-trimethylcyclopropanes (2). These isomeric cyclopropanes were formed from diazirine **1** and trimethylethylene by thermolysis at 45 °C in 28% yield[45] and a 1:30 isomer distribution. The products were purified by distillation at 70 °C/0.03 mmHg. The capillary GC retention times were 2.00 and 2.15 (major adduct) min: ^1H NMR (major isomer, $CDCl_3$, 400 MHz) δ 0.81, 0.90, 1.30 (*each*: s, 3 H, CMe), 0.90 (under singlet, 1 H, CH), 3.02 (s, 3 H, OMe), 7.25 (m, 5 H, Ph). Anal. Calcd for $C_{13}H_{18}O$: C, 82.04; H, 9.54. Found: C, 82.35; H, 9.80.

1-Methoxy-1-phenyl-2,2-dimethylcyclopropane (3). This compound was formed from diazirine **1** and isobutene by thermolysis at 45 °C in 21% yield.[45] It was purified by preparative GC at 115 °C with a He flow rate of 70 mL/min, retention time 11 min. The capillary GC retention time was 1.48 min: ^1H NMR (CCl_4, 60 MHz) δ 0.72 (s, 3 H, CMe), 0.52, 0.62 and 0.83, 0.93 (AB q, J = 6 Hz, 2 H, CH_2), 1.30 (s, 3 H, CMe), 3.07 (s, 3 H, OMe), 7.33 ("s", 5 H, Ph). Anal. Calcd for $C_{12}H_{16}O$: C, 81.76; H, 9.16. Found: C, 81.77; H, 9.16.

1-Methoxy-1-phenyl-2,3-*trans*-dimethylcyclopropane (4). This compound was formed from diazirine **1** and *trans*-butene by thermolysis at 45 °C in 24% yield.[45] It was purified by preparative GC at 140 °C with a He flow rate of 60 mL/min, retention time 8 min. The capillary GC retention time was 1.69 min: ^1H NMR (CCl_4, 60 MHz) δ 0.73 ("d", 3 H, CMe), 0.73–1.3 (m, 2 H, 2CH), 1.27 ("d", 3 H, CMe), 3.03 (s, 3 H, OMe), 7.30 ("s", 5 H, Ph). Anal. Calcd for $C_{12}H_{16}O$: C, 81.76; H, 9.16. Found: C, 81.98; H, 9.18.

1-Methoxy-1-phenyl-2-*n*-butylcyclopropanes (5). These isomeric compounds were formed from diazirine 1 and 1-hexene by thermolysis at 45 °C in 8.3% yield,[45] with an isomer distribution of 1:5.2. They were purified as a mixture by preparative GC at 170 °C with a He flow rate of 60 mL/min, retention time 10 min. The capillary GC retention times were 3.83 and 4.32 (major adduct) min: ^1H NMR ($CDCl_3$, 400 MHz) δ 0.70–1.70 (m's, Bu, and cyclopropyl CH_2 and CH), 3.11 (s, OMe,

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[38] Moss, R. A.; Mallon, C. B. *J. Am. Chem. Soc.* **1975**, *97*, 344.

[39] Moss, R. A.; Perez, L. A. *Tetrahedron Lett.* **1983**, *24*, 2719.

[40] Moss, R. A.; Guo, W.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1982**, *23*, 15.

[41] Moss, R. A.; Fedorynski, M.; Terpinski, J.; Denney, D. Z. *Tetrahedron Lett.* **1986**, *27*, 419.

[42] Hoffmann, R. W.; Lillienblum, W.; Dittrich, B. *Chem. Ber.* **1974**, *107*, 3395. Hoffmann, R. W.; Reiffen, M. *Ibid.* **1976**, *109*, 2565.

[43] Reiffen, M.; Hoffmann, R. W. *Chem. Ber.* **1977**, *110*, 37.

[44] Kmiecik-Ławrynowicz, G.; Moss, R. A., unpublished work.

[45] All yields are based on 3-bromo-3-phenyldiazirine and should be doubled to approximate the yield based on diazirine **1**.

minor adduct), 3.25 (s, OMe, major adduct), 7.22–7.40 (m, Ph). Anal. Calcd for $C_{14}H_{20}O$: exact mass 204.1514, found 204.1511.

1-Methoxy-1-phenyl-2-carbomethoxycyclopropanes (6). These isomeric compounds were formed from diazirine **1** and methyl acrylate (containing a trace of hydroquinone monomethyl ether as a stabilizer) by thermolysis at 45 °C in 8.9% yield[45] and a 1:4 isomer distribution. They were purified by Kugelrohr distillation at 40 °C/0.03 mmHg. Their capillary GC retention times were 3.59 and 4.91 (major adduct) min: ^{1}H NMR ($CDCl_3$, 400 MHz) δ major isomer 1.50 (m, 1 H, CH), 1.97 (t, J = 7.5 Hz, 1 H, CH), 2.12 (t, J = 7.5 Hz, CH), 3.20 (s, 3 H, OMe), 3.74 (s, 3 H, COOMe), 7.35 ("s", 5 H, Ph), minor isomer 1.50 (m, CH), 1.79 (t, J = 7.5 Hz, 1 H, CH), 2.33 ("t", J = 7.5 Hz, 1 H, CH), 3.14 (s, 3 H, OMe), 3.43 (s, 3 H, COOMe), 7.30 (m, 5 H, Ph). Anal. Calcd for $C_{12}H_{14}O_3$: exact mass 206.0943, found 206.0931.

1-Methoxy-1-phenyl-2-cyanocyclopropanes (7). These isomeric compounds were formed from diazirine **1** and acrylonitrile (stabilized as for acrylate) by thermolysis at 45 °C in 22% yield[45] and a 1:2.2 isomer distribution. They were purified by Kugelrohr distillation at 40 °C/0.03 mmHg. Their capillary GC retention times were 3.36 and 4.18 (major adduct) min: IR 2230 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.57–2.03 (5 multiplets, CH's, both isomers, 3 H), 3.17 (s, minor adduct), 3.32 (s, major adduct) (total 3 H, OMe's), 7.25–7.50 (m, 5 H, Ph). Anal. Calcd for $C_{11}H_{11}NO$: exact mass 173.0841, found 173.0824.

Competition Experiments. Diazirine **1** (~0.6 mmol in pentane) was added to a weighed, binary mixture of the two alkenes, cooled to −40 °C, and contained in a screw-top Carius tube. The alkenes were each present in at least 9-fold molar excess, relative to **1**. A magnetic stirring bar was added, the tube was sealed and covered with Al foil, and its contents were stirred at 25 °C for ~90 min, at which time the yellow-green color of **1** had bleached and N_2 evolution had ceased. The gross weight of the reaction vessel was checked several times to ensure that leakage of gaseous alkenes had not occurred. After completion of the reaction, the tube was cooled to −25 °C and opened, and the contents were warmed to ambient temperature, stirred for ~2 h, and analyzed by capillary GC using a Varian Model 3700 flame-ionization unit. Injector and detector temperatures were 250 and 300 °C, respectively. Other conditions are given above. The detector was calibrated with authentic samples of the products **2**–**7**. For further methodology, control experiments, and the method of calculating k_{rel}, see the Results section.

Absolute Rate Studies. The laser equipment and methodology are described in the Results section.

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Laser Flash Photolysis Study of Triplet States in Aligned Liquid Crystalline Media

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Abstract: A simple method for the laser flash photolysis study of aligned liquid crystals is reported. The formation of triplets of zinc tetraphenylporphyrin and 2-piperidinoanthraquinone in aligned nematic and isotropic phases of some commercially available cyanobiphenyl liquid crystals was studied. An observed increase in triplet–triplet absorption intensity in the nematic phase compared to the isotropic phase is entirely due to improved alignment and absorption of the polarized laser emission and contradicts a previously reported finding of enhancement of intersystem crossing efficiency. The variation of triplet lifetimes with temperature indicates that the microviscosity unlike the measured macroviscosity does not change drastically at the nematic–isotropic transition temperatures. At high laser intensities local melting of the nematic-to-isotropic phase was observed because of internal conversion–radiationless decay.

There have been a few reports on the use of thermotropic liquid crystals as solvents for various photochemical reactions.[1–8] In a laser flash photolytic study,[1] Levanon observed that the triplet absorption yield of zinc tetraphenylporphyrin (ZnTPP) in a magnetically aligned nematic biphenyl showed a marked enhancement below the clearing point of the nematic. This was attributed to the improved alignment of the optical transition and more significantly to an increased intersystem crossing efficiency in the ordered nematic phase. Such an observation could potentially be very important in the use of liquid crystalline solvents to selectively alter the photophysical and/or photochemical behavior of guest molecules. Very recently Leigh[5] investigated the unimolecular triplet decay of a series of alkoxypropiophenones in liquid crystalline phases. They believed that the inhibiting effect of an unaligned nematic liquid crystal solvent on a bond rotation (which is required for intramolecular triplet quenching) was primarily influenced by the microviscosity.

We have been interested in the laser flash photolysis study of various guest molecules in liquid crystalline solvents. One of the major problems involved in this system is the opacity of liquid crystals in the nonaligned state. In the present work, we report a simple method for the laser flash photolysis study of aligned liquid crystals. Using this methodology, we have looked into the temperature and phase dependent triplet formation of ZnTPP in some commercially available nematic liquid crystals in order to evaluate the potential effect of anisotropic and order properties of liquid crystals upon excited state–excited state or excited

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(1) Levanon, H. *Chem. Phys. Lett.* **1982**, *90*, 465.
(2) Gonen, O.; Levanon, H. *J. Phys. Chem.* **1985**, *89*, 1637.
(3) Leigh, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 6114.
(4) Leigh, W. J. *Can. J. Chem.* **1985**, *63*, 2736.
(5) Leigh, W. I. *Can. J. Chem.* **1986**, *64*, 1130.
(6) Anderson, V. C.; Craig, B. B.; Weiss, R. G. *J. Phys. Chem.* **1982**, *86*, 4642.
(7) Anderson, V. C.; Weiss, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 6628.
(8) Nerbonne, J. M.; Weiss, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 402.

0002-7863/87/1509-4349$01.50/0