anionic[21] species can have significant effects on observed structure-reactivity parameters in water.

Registry No. 1, 116724-74-4; H_2, 1333-74-0; D_2, 7782-39-0; T_2, 10028-17-8; H_2O, 7732-18-5.

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Direct Observational Studies of a Singlet Alkylcarbene: Methylmethoxycarbene, a Remarkably Selective Nucleophile

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Many carbenes have been spectroscopically characterized under matrix isolation conditions or by time-resolved methods in solution,[2] but very few *alkylcarbenes* have been *directly* observed. Facile 1,2-hydrogen migration[3,4] particularly limits the persistence of *singlet* alkylcarbenes, although several *triplet* alkylcarbenes, where spin barriers mitigate rearrangement, have been spectroscopically observed.[5] Electron donation from α-heteroatomic substituents stabilizes singlet carbenes; singlet methylcarbene should[3b] and does preferentially rearrange to ethylene, but methylchlorocarbene displays a rich intermolecular chemistry.[6] α-Oxygen (2p-2p overlap) stabilization is superior to that of α-chlorine (3p-2p overlap), so that methylmethoxycarbene is of special interest.[7,8]

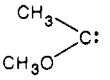
Now we report the direct spectroscopic observation of methylmethoxycarbene (**1**, MeCOMe) in *both* matrices and solution. Not only does the stabilization provided to this alkylcarbene by the methoxy substituent permit its observation but it also confers powerful, intermolecular nucleophilic selectivity.

Table I. Relative Reactivities of MeCOMe toward Alkenes at 25 °C[a]

alkene	k_{rel}
$Me_2C{=}CHMe$	2.13
$Me_2C{=}CH_2$	2.18
trans-$MeCH{=}CHMe$	1.00[b]
$CH_2{=}CHCOOMe$	362
$CH_2{=}CHCN$	686
$CH_2{=}CClCN$	22300

[a] The experimental relative reactivities, GC calibrations, and cross-check results will appear in the Ph.D. Thesis of B. K. Wilk. Error limits are ≤5%. [b] The data are normalized to *trans*-butene.

3-Methyl-3-methoxydiazirine (**2**)[9] was isolated in a nitrogen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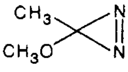
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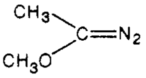
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$CH_3CH(OCH_3)_2$
4

matrix ($\mathbf{2}:N_2 \sim 1:800$) at 10 K and irradiated at 312 nm for 12 h. A photolabile intermediate was generated that had strongest IR bands at 1330, 1320, 1288, 1275, 1160, 1100, and 550 cm^{-1}. We assign these bands to MeCOMe in analogy to previous characterizations of alkoxycarbenes.[8] The carbene bands were accompanied by photoproduct bands that were augmented by additional broad band irradiation ($\lambda > 340$ nm). MeCOMe photoproducts, identified by IR, included acetone (~Me), methylvinyl ether (~H), and ketene and methane (Me-O fragmentation, followed by disproportionation) in an approximate ratio of 60:30:10 (%), respectively. A small amount of methylmethoxydiazomethane (**3**; 2020, 1260 cm^{-1}) was produced in the matrix by photoisomerization of **2**; it could be rapidly and *selectively* destroyed by irradiation at 465 nm.

UV-vis spectra of these irradiated matrices reveal a broad band centered at ~390 nm, with growth identical with that of the IR bands attributed to **1**. Importantly, the UV "action spectrum" for photochemical destruction of the IR bands of **1** matched the UV absorption spectrum, so that we attribute the 390-nm band to MeCOMe.[11,12] *No* UV-vis absorption corresponding to diazoalkane **3** (at ~465 nm) could be observed.

The MeCOMe assignment was confirmed by methanol trapping. Irradiation of **2** at 335 nm in a 4:1 2-methylbutane/MeOH glass at 20 K afforded the IR absorptions of MeCOMe (and photoproducts). Warming the glass to 80 K caused the disappearance of the carbene bands, together with the growth of IR bands due to acetal **4**.

Irradiation of pentane, isooctane, or acetonitrile *solutions* of **2** ($A_{380} \sim 1.2$) with a 14 ns, 70-90 mJ, 351-nm pulse from a XeF excimer laser[13] afforded a single transient signal in the 250-500-nm region, with a broad maximum between 370 and 400 nm.[14] The transient appeared within the laser pulse, and, in pentane, it decayed with first-order kinetics (quenching by **2**) with $k \sim 5 \times 10^5 - 2 \times 10^6\ s^{-1}$. The signal was not very intense, so that kinetic results are less precise than desired. Nevertheless, the solution transient absorption matched that of the matrix species and is assigned to MeCOMe.

The MeCOMe absorption could be quenched by MeOH, acrylonitrile, and α-chloroacrylonitrile in pentane solution at 20

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[6] Moss, R. A.; Mamantov, A. *J. Am. Chem. Soc.* **1970**, *92*, 6951.

[7] Indeed, the only well-characterized, directly observed (probably) singlet *alkylcarbene* of which we are aware is 4-oxatricyclo[3.2.1.$0^{2,7}$]octan-3-ylidene, which is Bredt's rule protected against ~H. Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1987**, *109*, 5029.

[8] Other oxacarbenes that cannot undergo ~H and are readily observed, stable singlets in matrices include methoxychlorocarbene and phenoxychlorocarbene: Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 99. Sheridan, R. S.; Kesselmayer, M. A. *J. Am. Chem. Soc.* **1984**, *106*, 436. Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 844.

[9] Moss, R. A.; Fedorynski, M.; Kmiecik-Ławrynowicz, G.; Terpinski, J. *Tetrahedron Lett.* **1986**, *27*, 2707. A more efficient conversion of 3-bromo-3-methyldiazirine to **2** involves reaction with NaOMe in DMF[10] at -30 °C for 25 min, followed by extraction of **2** ($\tau_{1/2} \sim 14.5$ min, hexane, 25 °C) with cold pentane from an ice water quench of the reaction mixture.

[10] Moss, R. A.; Włostowski, M.; Shen, S.; Krogh-Jespersen, K.; Matro, A. *J. Am. Chem. Soc.* **1988**, *110*, 4443.

[11] This is in agreement with the calculated spectrum; see below.

[12] We previously attributed the 390-nm absorbance of MeCOMe to **3**.[13] We revise this assignment in view of the evidence presented here.

[13] Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Ławrynowicz, G.; Włostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 4341.

[14] Close inspection reveals *two* closely spaced maxima, consistent with the presence of *trans*- and *cis*-**1**; see below.

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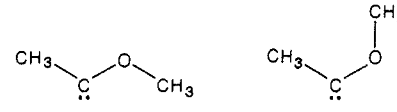
°C.[15] These experiments were monitored at 380 or 400 nm (with comparable results) and afforded bimolecular rate constants in the usual way.[16,17] With 0.002–0.034 M MeOH, curved plots[17] of k versus [MeOH] afforded the rate constant for the reaction of MeCOMe with *oligomeric* MeOH[17] as $7.0 \pm 0.8_2 \times 10^9$ M^{-1} s^{-1}, similar to the quenching of PhCOMe ($\sim 10^{10}$ M^{-1} s^{-1})[13] and much more rapid than the $(MeO)_2C$/MeOH reaction, for which $k = 2.5 \times 10^6$ M^{-1} s^{-1}.[10] Quenching with 0.1–3 M acrylonitrile gave $k = 1.5 \pm 0.1_3 \times 10^6$ M^{-1} s^{-1}, again similar to the analogous PhCOMe rate constant[13] and ~1000 times greater than that of $(MeO)_2C$.[10] With α-chloroacrylonitrile, quenching experiments gave $k \sim 1 \times 10^7$ M^{-1} s^{-1}, about 20 times greater than the comparable $(MeO)_2C$ rate constant.[10] Trimethylethylene did not quench the transient absorption of MeCOMe.

Thermolysis of diazirine **2** at 25 °C in trimethylethylene, isobutene, *trans*-butene, methyl acrylate, acrylonitrile, or α-chloroacrylonitrile gave the anticipated cyclopropanes in low (≤10%) isolated yields, based on the acetamidine precursor of **2**. GC analysis showed that the cyclopropanes and methylvinyl ether were the only significant non-azine products.[18] Structures were established by IR and NMR spectroscopy and by exact mass or elemental analysis.

Classical, product based competition reactions,[19] in which binary pairs of olefins were allowed to compete for an insufficiency of thermally generated MeCOMe, gave cyclopropane product mixtures that were analyzed by SE-30 capillary GC, with a calibrated flame ionization detector and an electronic integrator. The resulting relative reactivities, normalized to a *trans*-butene standard, appear in Table I.

The extraordinary nucleophilic selectivity of MeCOMe is obvious and is unsurpassed by previously reported carbenes.[13,20,21] Both the selectivity and spectral properties of MeCOMe are nicely rationalized by theoretical considerations.[22] The carbene should exist as trans and cis ground-state singlets.[23] *trans*-**1** is calculated[22] to be 8.6 kcal/mol more stable than *cis*-**1**. The transition state calculated for their interconversion is 31.3 kcal/mol above *trans*-**1**, so that, if both "isomers" are generated from **2**, cis–trans carbene interconversion would not be expected to occur during the MeCOMe lifetime in solution (<2 μs at 20 °C).



	trans-1	*cis*-1
ϵ_{LU}, eV[22]	4 04	3.86
ϵ_{HO}, eV[22]	-9.41	-8.96

We calculate[22] S_0–S_1 (σ^2–σ^1p^1) transitions for *trans*- and *cis*-**1** at 376 and 385 nm, respectively, and we do observe two closely spaced UV absorptions for **1** (e.g., 375 and 390 nm) in pentane solution. The IR absorptions of **1** in a nitrogen matrix at 10 K (see above) can be tentatively assigned to isomeric forms of MeCOMe. *trans*-**1** (λ^{max}_{calcd} 376 nm) is selectively destroyed by irradiation at 335 nm (IR: 1330, 1288, 1160, 1100, 550 cm^{-1}), and *cis*-**1** (λ^{max}_{calcd} 385 nm) is selectively destroyed by irradiation at 435 nm (IR: 1320, 1275 cm^{-1}).

Qualitatively, the combination of high-lying HOMO and LUMO in either isomer of **1** is precisely what is required for well expressed nucleophilic selectivity.[13] Indeed, the HOMO energies of **1** are comparable to those of PhCOMe,[13] while the LUMO energies are similar to those of $(MeO)_2C$.[10] By using the calculated[22] frontier molecular orbital energies[13,20] of **1** and available experimental orbital energies of the alkenes, we find that differential orbital energies[13,20] for the addition reactions of *both trans*- and *cis*-**1** are dominated by "nucleophilic" HOMO-**1**/LUMO-alkene interactions, in good accord with the experimental results.

The spectroscopic, computational, and kinetic studies of MeCOMe that we have described dramatically illustrate the extraordinary power of the methoxy substituent to alter the properties of an alkylcarbene.

Acknowledgment. We are grateful to the National Science Foundation, the Petroleum Research Fund (R.S.S.), and the A. P. Sloan Foundation (R.S.S.) for financial support. We thank A. Matro and Hong Fan for technical assistance.

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[15] Appropriate products are formed in the analogous preparative scale bimolecular reactions (i.e., **4** or cyclopropanes). In pentane alone, decomposition of **2**, gave (*E*,*E*)- and (*E*,*Z*)-azines [$(Me(MeO)C{=}N{-})_2$] that are most reasonably derived from the attack of **1** on **2**.

[16] Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576.

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

[18] The yield of methylvinyl ether formed upon decomposition of **2** in pentane alone was ~8%. The ether was the only non-azine product detected.

[19] Moss, R. A. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. I, p 153f.

[20] Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58.

[21] For the use of chloroacrylonitrile in carbenic selectivity experiments, see: Moss, R. A.; Fan, H.; Hadel, L. M.; Shen, S.; Włostowska, J.; Włostowski, M.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1987**, *28*, 4779.

[22] Ab initio calculations employed the GAUSSIAN 86 series of programs: Frisch, M.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Stewart, J. J. P.; Bobrowicz, F.; DeFrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fluder, E.; Pople, J. A. GAUSSIAN 86, Release C, Carnegie-Mellon University. Computational procedures included geometries, HF/6-31G*//6-31G*; HOMO/LUMO energies, HF/4-31G//STO-3G (to conform with previous usage);[13,20] S_0–T_1 separations and relative energies, MP3/6-31G*//6-31G*; and S_0–S_1 separations, HF/6-31G* geometries, singly excited configuration interaction, INDO/S model. See ref 10 for more detail and references.

[23] Calculated[22] vertical S_0–T_1 separations are 40.7 (*trans*-**1**) and 32.4 (*cis*-**1**) kcal/mol.

Synthesis and Stabilization of Tantalum-Coordinated Dihydroxyacetylene from Two Reductively Coupled Carbon Monoxide Ligands

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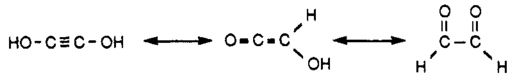
In 1834 Justus Liebig reported the reductive coupling of carbon monoxide by potassium metal to form "potassium carbonyl",[1] later shown to contain the potassium salt of acetylenediolate, $K_2(^-O{-}C{\equiv}C{-}O^-)$.[2] Many attempts have subsequently been made to obtain useful organic compounds from alkali metal or electrochemical CO reductions, but in general the products are unstable or intractable.[3] Although the conjugate acid of acetylenediolate, dihydroxyacetylene, has been observed in the gas phase by using neutralization–reionization mass spectrometry,[4] solutions of dihydroxyacetylene would presumably be unstable, tautomerizing to hydroxyketene or glyoxal, eq 1.[5] Previously we



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