papers.[2,3] Differing from such stable aromatic azo compounds as benzo[*c*]cinnoline and indazole, **1** is too labile to isolate in the solid state at room temperature and turn into the deep blue-purple compound which is presumed to be the product from polymerization or self-condensation of **1**.[1,9] Addition of protic solvents, e.g., methanol, into the dilute solution of **1** gives the adduct of **1** with the protic solvents which was not definitely identified because of its lability.[10]

In conclusion, unusual properties of **1** as compared with typical aromatic azo compounds would be explained in the terms of the lack of usual double bond character for the N═N bond, which was elucidated by the IR spectroscopic studies.

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(9) Deep blue-purple solids having λ_{max} ca. 550 nm in the absorption spectrum. It was not characterized because it gave a wide streak on thin-layer chromatography and showed complicated peaks on ^1H and ^{13}C NMR spectra.

(10) In dilute solutions (e.g., ether:2-methylbutane:ethanol = 5:5:2) at room temperature it has characteristic absorption maxima at 331, 317, and 304 nm.

Dimethoxycarbene: Direct Observation of an Archetypal Nucleophilic Carbene[†]

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Difluorocarbene and methoxychlorocarbene are representative electrophilic and ambiphilic carbenes[2] that have been extensively studied and directly observed.[3,4] Dimethoxycarbene (DMC), perhaps the archetypal nucleophilic carbene,[2] is most frequently generated by pyrolyses of 7,7-dimethoxynorbornadiene derivatives.[5] Although much has been learned about its chemistry, these generative conditions are not easily adapted to *direct observation* of DMC.

We are therefore pleased to report the preparation of 3,3-dimethoxydiazirine (**1**), the facile generation of DMC,[6] the matrix isolation and ambient temperature UV spectra of DMC, and initial absolute kinetic studies of the carbene's reactions with methanol and alkenes. There have been many direct studies of triplet arylcarbenes[7] and singlet arylhalocarbenes[8,9] in solution, but this is the first observational study of a nucleophilic carbene.

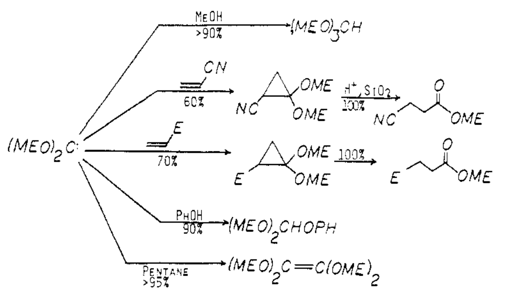


Figure 1. Reactions of DMC generated thermally from diazirine **1** at 25 °C; ME = methyl, PH = phenyl, E = COOMe. See text for discussion.

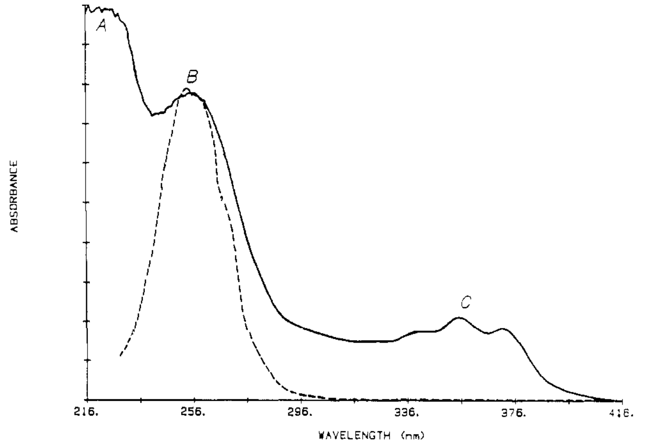
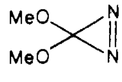


Figure 2. UV spectra of DMC in a 3-methylpentane glass at 77 K (solid line) and in pentane solution at 25 °C (dashed line). See text for assignments and discussion.



1

(MeO)$_2$C═C(OMe)$_2$

2

3-Chloro-3-methoxydiazirine[10] was converted to **1** by exchange[6b,9,11] with excess NaOMe in DMF at −30 to −50 °C for 30 min. Rapid extraction with cold pentane of a crushed ice/water quench of the reaction mixture, drying ($CaCl_2$, −20 °C, 20 min), and filtration through silica gave ~60% of diazirine **1** as a ~0.07 M pentane solution. Analogous solutions were used for all further experiments. The identification of **1** rests on its method of preparation,[6b,9] characteristic[10] UV spectrum (λ_{max} 338 sh, 358, 372 nm), and decomposition products (see below).

Thermal decomposition of **1** in pentane was monitored at 372 nm over eight temperatures between 15 and 50 °C. The kinetics were first order, with $k = 5.43 \times 10^{-4}\ s^{-1}$, $\tau_{1/2} \sim 21$ min at 25 °C,[12] and $E_a = 18.9$ kcal/mol. The sole product was carbene dimer **2**,[13] identical in GC retention time and NMR spectrum to an authentic sample.[5e]

[†] Dedicated to Professor Gerhard L. Closs on the occasion of his 60th birthday.

(1) Visiting Scientist on leave from the Politechnika, Warsaw, Poland.

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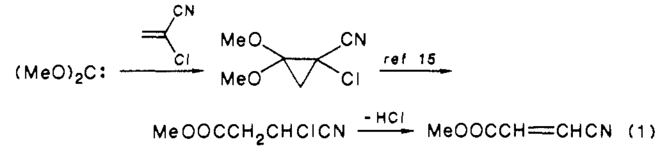
(12) Diazirine **1** is less stable than 3-methoxy-3-phenoxydiazirine, which has $\tau_{1/2} \sim 64$ min under comparable conditions.[6b]

(13) If methanol or water is present, methyl orthoformate is also formed.

A summary of characteristic[5] DMC reactions, upon thermal generation from **1** at 25 °C, appears in Figure 1, with yields based on **1**. The orthoformates derived from methanol or phenol were high yield, sole products formed in pentane/ether solution. They were identified by GC and NMR comparisons with authentic samples.[14] Cyclopropanes were derived in good yields from DMC additions to acrylonitrile and methyl acrylate. These primary products were isolated by kugelrohr distillation at 25 °C/0.1 mmHg and characterized by NMR, IR, and mass spectroscopy. The cyclopropanes readily opened to succinic ester derivatives in precedented, SiO_2-catalyzed, hydrolytic reactions.[15] Reaction of DMC with chloroacrylonitrile (not shown in Figure 1) led to 70% of isolated *trans-β*-cyanoacrylic acid methyl ester,[16] presumably formed via opening of the unisolated cyclopropane, followed by (autocatalytic) loss of HCl, eq 1.



A clear 3-methylpentane glass of diazirine **1** ($A_{372} \sim 2.3$) was irradiated at 77 K for 10 min with uranium glass-filtered light ($\lambda > 330$ nm) from an Osram focused XE mercury lamp, affording the UV spectrum shown in Figure 2 (solid line). Absorptions at C and A are due to diazirine **1** and dimer **2**,[17] respectively, whereas we assign absorption B at 255 nm to DMC. The DMC absorption is stable for at least 30 min at 77 K but disappears when the matrix is thawed and refrozen, a process that greatly enhances the dimer absorption. Capillary GC analysis of the thawed matrix showed only **2**.

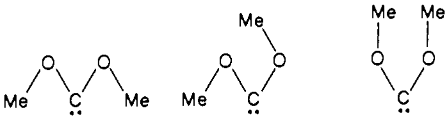
When a pentane solution of **1** ($A_{372} \sim 1.0$) was subjected to a 14-ns, 90-mJ, 351-nm pulse from our XeF excimer laser,[9] a transient absorption appeared within the time period of the pulse. Figure 2 (dashed line) shows a point-by-point trace of this signal, taken at 3-nm intervals, that corresponds very closely to the matrix DMC absorption. No other transients appeared below 500 nm, but a very weak absorption was observed in the 515–570-nm region.[18]

The 255-nm transient signal of DMC in pentane decayed very slowly at 25 °C ($\tau_{1/2} \sim 2$ ms),[19] with clear second-order kinetics (i.e., $1/A$, but not $\ln A$, was linear with time), and dimer **2** was formed. DMC thus decayed about 100 times more slowly than MeOCPh ($\tau \sim 15$–30 μs under comparable conditions),[9] in keeping with its anticipated greater stabilization (see below).

The DMC transient was quenched by methanol, chloroacrylonitrile, or acrylonitrile. Absolute rate constants for the alkene reactions were obtained in the standard way,[20] but the dependence of the quenching rate constants on [MeOH] was curved concave upward, as expected.[9,21] Applying the method of Griller et al.,[21] we found $k_{abs} = 2.5 \times 10^6$ M^{-1} s^{-1} for the reaction of DMC with *oligomeric* methanol, about 1000 times less than k_{abs} for the analogous reactions of MeOCPh[9] or PhCCl.[21]

An excellent linearity between k_{obsd} and [olefin] was observed in the DMC/chloroacrylonitrile reaction,[22] with $k_{abs} = 5.0 \times 10^5$ M^{-1} s^{-1}. With acrylonitrile, much slower quenching (near the limit of our present electronics) was observed, with $k_{abs} \sim 10^3$ M^{-1} s^{-1}. These k_{abs} values for DMC additions are 70 and ~1700 times smaller than those for the comparable MeOCPh reactions.[9] In keeping with its nucleophilic character,[2,5] DMC was not quenched by either 2.7 M tetramethylethylene or 3.2 M trimethylethylene within the time domain of our apparatus ($k_{abs} < 10^3$ M^{-1} s^{-1}).

Our ab initio calculations on DMC employed the GAUSSIAN 86 programs.[23] Singlet conformers **3a–c** were geometrically optimized at the Hartree–Fock level with the split valence plus polarization function 6-31G* basis set.



	3a	**3b**	**3c**
ϵ_{LU}, eV[24a]	4.34	4.49	4.35
ϵ_{HO}, eV[24a]	-10.62	-10.38	-9.64
E_{rel}, kcal/mol[24b]	0.00	1.56	21.34

All-trans conformer **3a** and cis-trans conformer **3b** should coexist at low temperature[25] (the barrier[26] to their interconversion is 15.8 kcal/mol above **3a**), but *all-cis*-**3c** is at a much higher relative energy. The high-lying LUMO (and HOMO) energies calculated for DMC are responsible for its nucleophilicity.[2,9] Indeed, the rate of dimerization should depend on a carbene's HOMO–LUMO differential orbital energy (15.0 eV for DMC), so that DMC's "slow" dimerization is likely related to the magnitude of this $\Delta\epsilon$ and to the relative inaccessibility of its LUMO. Similarly, the "slow" dimerization of CF_2[3d,e] ($\Delta\epsilon = 15.3$ eV[24c]), and its electrophilicity, can be traced to its very low-lying HOMO.[9]

Other noteworthy calculational results for DMC include the following: (a) excited singlet states, corresponding to HOMO → LUMO ($\sigma^2 \rightarrow \sigma^1 p^1$) excitation, calculated at 262 nm (109 kcal/mol; **3b**) and 275 nm (104 kcal/mol; **3a**) [cf., the observed DMC absorption at 255 nm, 112 kcal/mol], at the HF/6-31G* optimized geometries with singly excited configuration interaction within the semiempirical INDO/S model;[27] and (b) lowest triplet states for **3a** and **3b** calculated 76.3 and 76.7 kcal/mol above their respective ground states (at the ab initio level) including correlation energy corrections to second order in Møller–Plesset theory (MP2/6-31G*//6-31G*).[23] Clearly, the chemistry of DMC reported here is to be associated with its ground-state singlet.

The ready accessibility of DMC from a spectroscopy-compatable precursor, together with its extraordinary longevity in solution and facile UV monitoring, now make possible definitive examinations of the structure and reaction energetics of this archetypal, stabilized, nucleophilic carbene.

Acknowledgment. We are grateful to the National Science Foundation for financial support. We thank Professor Harvey Schugar for assistance in determining the matrix UV spectrum of DMC, Dr. Michał Fedorynski for initial studies toward the synthesis of **1**, and Dr. John Westbrook for computational assistance.

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(14) $(MeO)_2CHOPh$ was prepared by the method of Barbot et al. (Barbot, F.; Poncini, L.; Randrianoelina, B.; Miginiac, P. *J. Chem. Res. M* **1981**, 4016, Table 6).

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(17) We observe λ_{max} 218 nm for **2** in pentane solution.

(18) The identity of this transient is unknown, but it could be the photolytically generated diazo isomer of **1**, $(MeO)_2C{=}N_2$; it is quenched by methanol.

(19) An aqueous $NiSO_4$ filter was placed in front of the Xe monitoring lamp to prevent adventitious photolysis of **1**.

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(24) (a) To conform with previous usage,[24c] the values are HF/4-31G//STO-3G. (b) These are HF/6-31G*//6-31G* values. The energy separation between **3a** and **3b** is 0.36 kcal/mol at the MP2/6-31G*//6-31G* level. (c) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770.

(25) Cis/trans isomerism is a characteristic feature of oxacarbenes that results from strong oxygen lone pair → carbene 2p (LUMO) delocalization.[4c,6b,9]

(26) A methyl group was oriented perpendicular to the carbenic OCO plane, and the molecular geometry was optimized under this constraint.

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