structural role of S$_b$, extended Hückel MO calculations were performed on [Nb$_6$S$_{17}$]$^{4-}$,[26] with these findings: (i) the interaction of Nb$_6$S$_{16}$$^{2-}$ and S$_b$$^{2-}$ affords a stabilization of ~1.9 eV over the isolated fragments; (ii) the overlap populations of Nb(1)–S$_t$ (0.58), Nb(1)–μ_3-S $\simeq$ Nb(1)–S$_b$ (0.23), Nb(2)–S$_{\text{terminal}}$ (0.60), Nb(2)–μ_3-S (0.28), Nb(2)–μ_2-S (0.36), and Nb(2)–S$_b$ (0.11) suggest that Nb(2–6)–S$_b$ interactions are significant, with a bond order slightly less than one-half that of the Nb(1)–S$_b$ bond. These results indicate that the S$_b$ atom is an integral part of the [M$_6$S$_{17}$]$^{4-}$ structure, which is the first example of a 16-atom C_{5v} cage. Full details of the structural and electronic properties of [M$_6$S$_{17}$]$^{4-}$ will be provided subsequently. The reactivity properties of these species are under investigation.

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Supplementary Material Available: X-ray structural data for (Et$_4$N)$_4$[Nb$_6$S$_{17}$]·3MeCN—positional and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Photochemical Wolff Rearrangement of a Triplet Ground-State Carbene

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The mechanism of the photochemical Wolff rearrangement is of special interest because of its importance in photolithography.[1] Stereochemical[2,3] and CIDNP[3] evidence is consistent, in most cases, with concerted loss of nitrogen and migration of the carbon–carbon bond.[4] Singlet α-ketocarbenes have been suggested as intermediates in Wolff rearrangements in which oxirene intermediates are believed to be involved and in reactions in which nitrogen loss is considered to occur before rearrangement.[4,5] Relatively few α-ketocarbenes have been studied spectroscopically, but those studied have triplet ground states.[6-9] In all cases, except perfluoro-2-oxo-3-butylidene, triplet α-ketocarbenes do not undergo the Wolff rearrangement. Triplet α-ketocarbenes produced

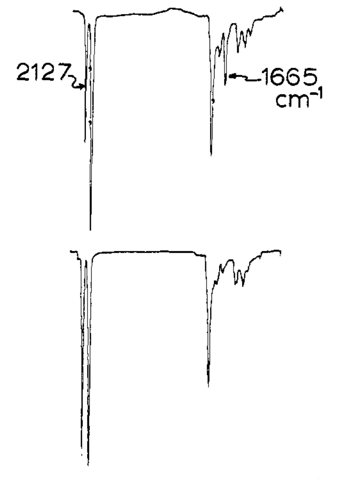
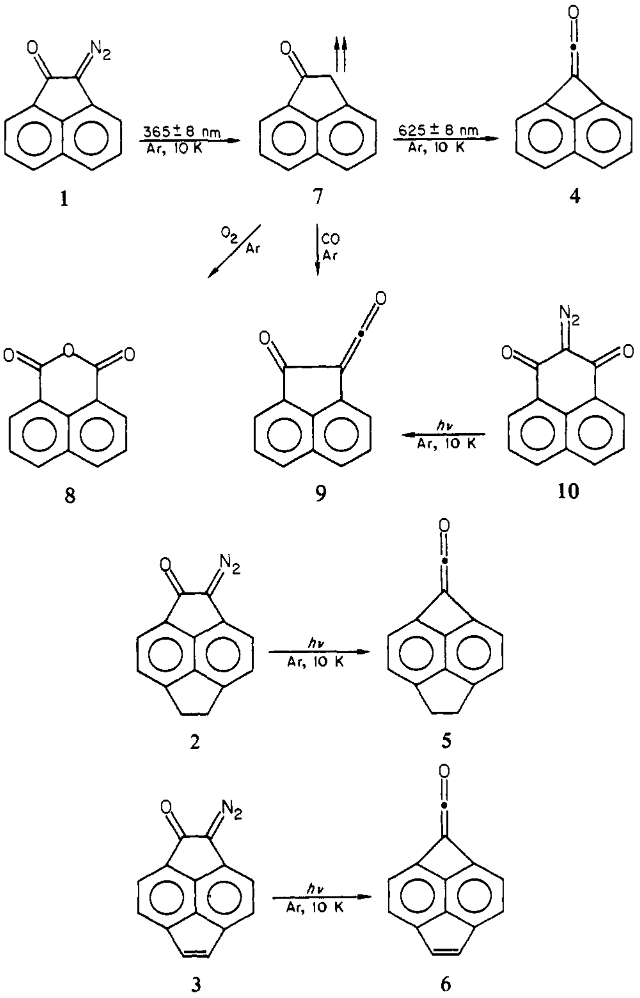


Figure 1. Top: Infrared spectrum (2200–1500 cm^{-1}) of diazo ketone **1** matrix isolated in argon after irradiation (365 ± 8 nm) for 45 min. Ketene **4** (2127 cm^{-1}) and α-ketocarbene **7** (1665 cm^{-1}) are visible. The bands at 2085 and 1702 cm^{-1} are due to diazo ketone **1**. Botton: The same sample after irradiation (625 ± 8 nm) for 182 min. The disappearance of the α-ketocarbene **7** and the concomittant increase in the ketene **4** are readily apparent.

Scheme I



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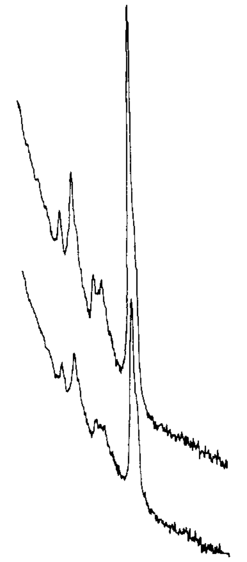
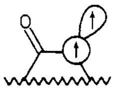


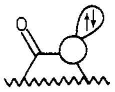
Figure 2. Top: Ultraviolet spectrum (520–700 nm) of α-ketocarbene **7** prepared by irradiation (365 ± 8 nm, 45 min) of **1** in an argon matrix. Bottom: The same sample after irradiation (625 ± 8 nm) for 62 min showing the decrease in α-ketocarbene.

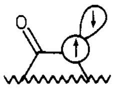
by photosensitized decomposition of α-diazoketones also do not give Wolff rearrangement.[4-6]

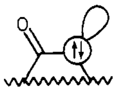
We sought a system in which the chemistry and spectroscopy of an α-ketocarbene could be studied. Increasing strain in the transition state for ring contraction should suppress Wolff rearrangement. Diazoketones **1**, **2**, and **3** seemed ideal precursors that impose increasingly severe strain limitations. Irradiations (>338 nm)[17] of each of these diazoketones matrix isolated in argon at 10–15 K gave clean Wolff rearrangement to the ketene (Scheme I) (**4**, 2127 cm^{-1}; **5**, 2127 cm^{-1}; **6**, 2128 cm^{-1}). Diazo ketone **1** gives no Wolff rearrangement product in solution either thermally or photochemically.[12,13] Irradiation of **1**, **2**, and **3** does not give the ketenes unless they are isolated in an inert matrix. Irradiation of **1** (365 ± 8 nm)[17] matrix isolated in argon at 10 K gives the α-ketocarbene **7** as the sole primary product (see trapping evidence below). The α-ketocarbene is characterized by its infrared spectrum (1665, 1015, and 767 cm^{-1}, (Figure 1), its ultraviolet spectrum (λ_{max} 621.3, 597.1, 590.3, 573.4, and 563.2 nm, Figure 2), and its electron spin resonance spectrum ($D/hc = 0.407$ cm^{-1}, $E/hc = 0.0270$ cm^{-1}, Z_1 990, X_2 4491, Y_2 5538, and Z_2 7632 G). The ground state of **7** is established as a triplet by a linear Curie law plot in the temperature range 18–30 K. The chemical identity of **7** is confirmed by trapping with oxygen in argon giving 1,8-naphthalic anhydride (**8**, identified by IR comparison with an authentic sample in argon) and with carbon monoxide in argon giving ketoketene **9**. The structure of **9** was established by independent synthesis from **10**. In the oxygen-trapping experiment, only a trace of ketene **4** was observed. The α-ketocarbene **7** is thus the primary photoproduct from diazoketone **1**. Experiments with infrared monitoring show initial formation (365 ± 8 nm) of the α-ketocarbene with subsequent photochemical conversion of this intermediate to ketene **4**. When **7** was irradiated at longer wavelength (625 ± 8 nm), the bands at 1665, 1015, and 767 cm^{-1} disappeared, and the bands characteristic of ketene **4** increased (Figure 1). The ultraviolet absorption (Figure 2) and the ESR signal due to **7** also disappear on irradiation at 625 ± 8 nm. Diazo ketone **1** is completely stable to irradiation under these conditions.

The yield of ketene **4** (measured by the intensity of the band at 2127 cm^{-1}) is inversely proportional to the concentration of oxygen or carbon monoxide in the matrix. Two conclusions come from this observation. First, ground-state (T_0) **7** is the only product


T_0


S'


S''


S'''

from S_1 diazo ketone, and second, under these conditions all of the observed Wolff rearrangement proceeds via **7** (T_0). Conversion of **7** to **4** is initiated by $T_0 \rightarrow T_1$ excitation of **7**. The energy of this transition is 46 kcal/mol. Calculations predict high barriers for 1,2-shifts in T_0 methylcarbene[14] but no barrier for Wolff rearrangement in the S_1 state of formylcarbene.[15] This system is conformationally mobile and rearrangement via S_1 involves rotation about the C–C bond. α-Ketocarbene **7** is not conformationally mobile, and bond migration is rigorously confined to the plane of the molecule. The lowest closed-shell singlet state (S')[16] of **7** which corresponds to S_1 in $H\ddot{C}CHO$) is inappropriate for in-plane rearrangement because the in-plane hybrid orbital is filled. In fact, S''' is the ideal configuration for in-plane bond migration because it has a vacant in-plane orbital, and we suggest that intersystem crossing $T_1 \rightarrow S'''$ occurs with rapid rearrangement of **7** (S''') to **4**. The S''' state in α-ketocarbenes is stabilized by delocalization of the electron pair into the carbonyl π-system.

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Registry No. **1**, 2008-77-7; **2**, 87985-99-7; **3**, 87986-00-3; **4**, 82515-17-1; **5**, 86998-10-9; **6**, 87016-12-4; **7**, 2235-15-6.

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(17) Irradiations were carried out with an ILC Technology LX300UV 300W high-pressure xenon arc lamp. Wavelength control was provided by either cut-off filters (0% transmittance of wavelengths shorter than the specified value) or a Kratos GM252-20 high-intensity quarter meter grating monochromator (16-nm band-pass centered at the specified value).

Mechanism of Ziegler–Natta Polymerization of Acetylene: A Nutation NMR Study

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In spite of the widespread commercial application of Ziegler–Natta catalysis in olefin polymerization, the mechanism of the fundamental carbon–carbon bond-forming reaction in this process is not well understood.[1] Currently available data do not distinguish between the more traditional four-center olefin insertion mechanism of Cossee and Arlman[2] and the recent metallacycle proposal of Green and co-workers.[3]

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