

structural role of  $S_b$ , extended Hückel MO calculations were performed on  $[Nb_6S_{17}]^{4-}$  with these findings: (i) the interaction of  $Nb_6S_{16}^{2-}$  and  $S_b^{2-}$  affords a stabilization of  $\sim 1.9$  eV over the isolated fragments; (ii) the overlap populations of  $Nb(1)-S_i$  (0.58),  $Nb(1)-\mu_3-S \approx Nb(1)-S_b$  (0.23),  $Nb(2)-S_{i\text{terminal}}$  (0.60),  $Nb(2)-\mu_3-S$  (0.28),  $Nb(2)-\mu_2-S$  (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  $[M_6S_{17}]^{4-}$  structure, which is the first example of a 16-atom  $C_{3v}$  cage. Full details of the structural and electronic properties of  $[M_6S_{17}]^{4-}$  will be provided subsequently. The reactivity properties of these species are under investigation.

**Acknowledgment.** This research was supported by NSF Grant CHE 81-06017. X-ray and NMR equipment used in this research were obtained by NSF Grants CHE 80-00670 and CHE 80-08891. We thank S. Rubenstein and Dr. Jay Dorfman for assistance with MO calculations.

**Supplementary Material Available:** X-ray structural data for  $(Et_4N)_4[Nb_6S_{17}]\cdot 3MeCN$ —positional and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

(26) Atom coordinates were averaged to  $C_{3v}$  symmetry. Method: Ammeter, J. H.; Bürgi, H.-B.; Thibault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. Parameters: Summerville, R. H.; Hoffmann, R. *Ibid.* **1976**, *98*, 7240. Hughbanks, T.; Hoffmann, R. *Ibid.* **1983**, *105*, 1150.

## Photochemical Wolff Rearrangement of a Triplet Ground-State Carbene

Richard A. Hayes, Thomas C. Hess, Robert J. McMahon, and Orville L. Chapman\*

Department of Chemistry and Biochemistry  
University of California, Los Angeles, California 90024

Received September 9, 1983

The mechanism of the photochemical Wolff rearrangement is of special interest because of its importance in photolithography.<sup>1</sup> Stereochemical<sup>2,3</sup> and CIDNP<sup>3</sup> evidence is consistent, in most cases, with concerted loss of nitrogen and migration of the carbon-carbon bond.<sup>4</sup> Singlet  $\alpha$ -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.<sup>4,5</sup> Relatively few  $\alpha$ -ketocarbenes have been studied spectroscopically, but those studied have triplet ground states.<sup>6-9</sup> In all cases, except

(1) Pacansky, J. *Polym. Eng. Sci.* **1980**, *20*, 1049-1053. Pacansky, J.; Lyster, J. R. *IBM J. Res. Dev.* **1979**, *23*, 42-55. Stinson, S. C. *Chem. Eng. News* **1983**, *61*, 7-12.

(2) Kaplan, F.; Meloy, G. K. *J. Am. Chem. Soc.* **1966**, *88*, 950-956. Kaplan, F.; Mitchell, M. L. *Tetrahedron Lett.* **1979**, 759-762.

(3) Roth, H. D.; Mannion, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 3392-3393. Roth, H. D. *Acc. Chem. Res.* **1977**, *10*, 85-91.

(4) For a general review, see: Meier, H.; Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32-43.

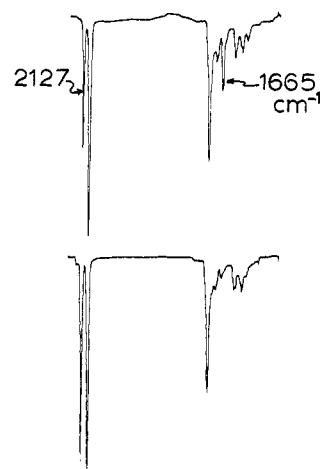
(5) Tomioka, H.; Okuno, H.; Kondo, S.; Izawa, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7123-7125.

(6) Trozzolo, A. M.; Fahrenholtz, S. R. *Abstr. of Pap.-Am. Chem. Soc. 151st 1966*, K23. Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329-335.

(7) Murai, H.; Torres, M.; Strausz, O. P. *Chem. Phys. Lett.* **1980**, *70*, 358-360.

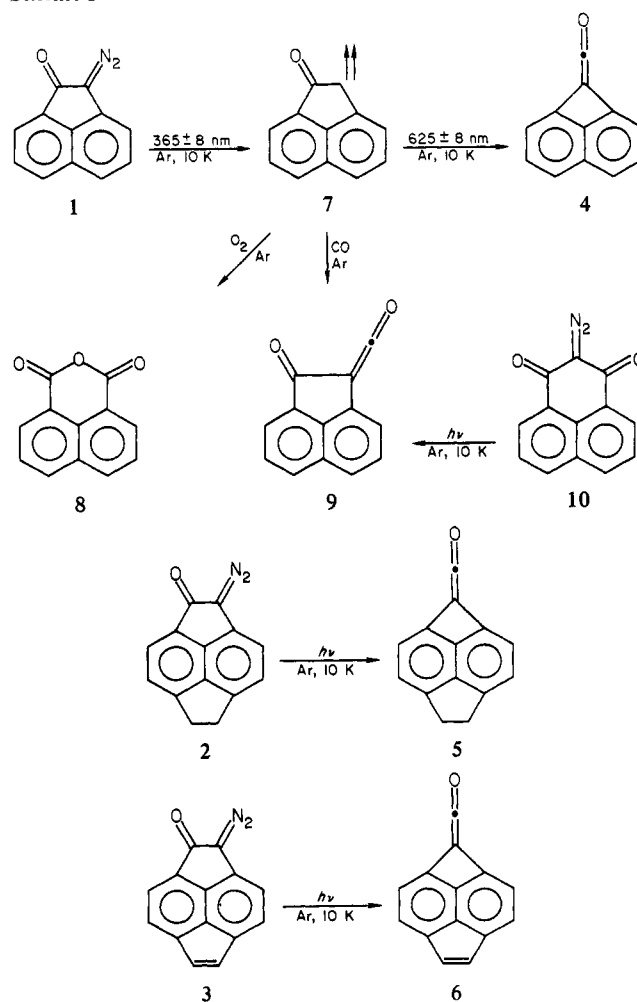
(8) The  $D$  value for dibenzoylmethylene is quite small compared to those of other  $\alpha$ -ketocarbenes (including 7 vide infra)<sup>6,9</sup> and other  $\alpha$ -carbonyl-carbenes.<sup>10</sup>

(9) Murai, H.; Ribo, J.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1981**, *103*, 6422-6426. Torres, M.; Bourdelande, J. L.; Clement, A.; Strausz, O. P. *J. Am. Chem. Soc.* **1983**, *105*, 1698-1700.



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

Scheme I

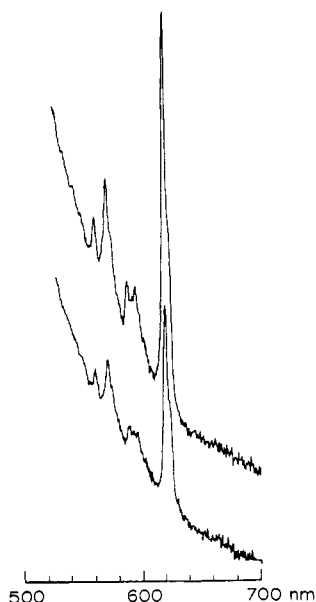


perfluoro-2-oxo-3-butyldiene, triplet  $\alpha$ -ketocarbenes do not undergo the Wolff rearrangement. Triplet  $\alpha$ -ketocarbenes produced

(10) Hutton, R. S.; Roth, H. D. *J. Am. Chem. Soc.* **1978**, *100*, 4324-4325.

(11) The syntheses of **1**, **2**, and **3** are described in: Hayes, R. A. Ph.D. Dissertation, University of California, Los Angeles, CA, 1982.

(12) Trost, B. M.; Kinson, P. L. *Tetrahedron Lett.* **1973**, 2675-2678.



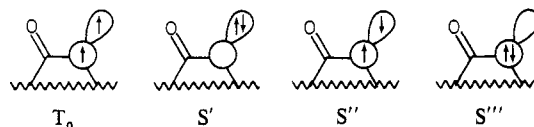
**Figure 2.** Top: Ultraviolet spectrum (520–700 nm) of  $\alpha$ -ketocarbene **7** prepared by irradiation ( $365 \pm 8$  nm, 45 min) of **1** in an argon matrix. Bottom: The same sample after irradiation ( $625 \pm 8$  nm) for 62 min showing the decrease in  $\alpha$ -ketocarbene.

by photosensitized decomposition of  $\alpha$ -diazoketones also do not give Wolff rearrangement.<sup>4–6</sup>

We sought a system in which the chemistry and spectroscopy of an  $\alpha$ -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)<sup>17</sup> of each of these diazoketones matrix isolated in argon at 10–15 K gave clean Wolff rearrangement to the ketene (Scheme I) (**4**,  $2127\text{ cm}^{-1}$ ; **5**,  $2127\text{ cm}^{-1}$ ; **6**,  $2128\text{ cm}^{-1}$ ). Diazo ketone **1** gives no Wolff rearrangement product in solution either thermally or photochemically.<sup>12,13</sup> Irradiation of **1**, **2**, and **3** does not give the ketenes unless they are isolated in an inert matrix. Irradiation of **1** ( $365 \pm 8$  nm)<sup>17</sup> matrix isolated in argon at 10 K gives the  $\alpha$ -ketocarbene **7** as the sole primary product (see trapping evidence below). The  $\alpha$ -ketocarbene is characterized by its infrared spectrum ( $1665$ ,  $1015$ , and  $767\text{ cm}^{-1}$ , (Figure 1), its ultraviolet spectrum ( $\lambda_{\text{max}}$   $621.3$ ,  $597.1$ ,  $590.3$ ,  $573.4$ , and  $563.2\text{ nm}$ , Figure 2), and its electron spin resonance spectrum ( $D/hc = 0.407\text{ cm}^{-1}$ ,  $E/hc = 0.0270\text{ cm}^{-1}$ ,  $Z_1$   $990$ ,  $X_2$   $4491$ ,  $Y_2$   $5538$ , and  $Z_2$   $7632\text{ G}$ ). 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  $\alpha$ -ketocarbene **7** is thus the primary photoproduct from diazoketone **1**. Experiments with infrared monitoring show initial formation ( $365 \pm 8\text{ nm}$ ) of the  $\alpha$ -ketocarbene with subsequent photochemical conversion

of this intermediate to ketene **4**. When **7** was irradiated at longer wavelength ( $625 \pm 8\text{ nm}$ ), the bands at  $1665$ ,  $1015$ , and  $767\text{ cm}^{-1}$  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  $625 \pm 8\text{ nm}$ . Diazo ketone **1** is completely stable to irradiation under these conditions.

The yield of ketene **4** (measured by the intensity of the band at  $2127\text{ cm}^{-1}$ ) 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



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  $46\text{ kcal/mol}$ . Calculations predict high barriers for 1,2-shifts in  $T_0$  methylcarbene<sup>14</sup> but no barrier for Wolff rearrangement in the  $S_1$  state of formylcarbene.<sup>15</sup> This system is conformationally mobile and rearrangement via  $S_1$  involves rotation about the C–C bond.  $\alpha$ -Ketocarbene **7** is not conformationally mobile, and bond migration is rigorously confined to the plane of the molecule. The lowest closed-shell singlet state ( $S'$ )<sup>16</sup> of **7** which corresponds to  $S_1$  in  $\text{H}\ddot{\text{C}}\text{CHO}$  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  $\alpha$ -ketocarbenes is stabilized by delocalization of the electron pair into the carbonyl  $\pi$ -system.

**Acknowledgment.** This research was supported by Grant CHE81-11196 from the National Science Foundation and a grant from the International Business Machine Corporation. Fellowships (R.J.M.) were provided by the National Science Foundation and the International Business Machine Corporation.

**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.

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

T. C. Clarke\* and C. S. Yannoni\*

IBM Research Laboratory  
San Jose, California 95193

T. J. Katz\*

Department of Chemistry, Columbia University  
New York, New York 10027

Received August 11, 1983

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.<sup>1</sup> Currently available data do not distinguish between the more traditional four-center olefin insertion mechanism of Cossee and Arlman<sup>2</sup> and the recent metallacycle proposal of Green and co-workers.<sup>3</sup>

(1) For a recent discussion and leading references, see: Soto, J.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4479–4480.

(2) Cossee, J. J. *Catal.* **1964**, *3*, 80–88. Arlman, E. J. *Ibid.* **1964**, *3*, 89–98. Arlman, E. J.; Cossee, P. *Ibid.* **1964**, *3*, 99–104.

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(14) Harding, L. B. *J. Am. Chem. Soc.* **1981**, *103*, 7469–7475. See also: Bouma, W. J.; Nobes, R. H.; Radom, L.; Woodward, C. E. *J. Org. Chem.* **1982**, *47*, 1869–1875. Kohler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1982**, *104*, 5884–5889. Altmann, J. A.; Csizmadia, I. G.; Yates, K. *J. Am. Chem. Soc.* **1974**, *96*, 4196–4201.

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(16) The carbene singlet states are designated  $S'$ ,  $S''$ , and  $S'''$  because their position in the singlet manifold relative to singlet states of the naphthalene chromophore is not known. The energies increase in the order  $S' < S'' < S'''$ .

(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).