

**Table I.**  $G(\text{H}_2\text{S})$  in the  $\gamma$ -Radiolysis of Dithiothreitol at pH 4 and  $20 \pm 1^\circ\text{C}$  at Different Dose Rates<sup>a</sup>

[DTT], M	$1.9 \times 10^{-1}$ , Gy s <sup>-1</sup>	$2.6 \times 10^{-2}$ , Gy s <sup>-1</sup>	$2.8 \times 10^{-3}$ , Gy s <sup>-1</sup>
$5 \times 10^{-4}$		12.2	31.6
$1 \times 10^{-3}$	3.6	11.2	32.3
$3 \times 10^{-3}$		11.3	31.4
$6 \times 10^{-3}$		11.6	32.3
$8 \times 10^{-3}$		11.7	31.1
$1 \times 10^{-2}$		10.8	31.0

<sup>a</sup>At the highest dose rate the dose did not exceed 55 Gy, at the lowest dose rate 10 Gy.

( $2k_{15} = 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at pH 4)<sup>6</sup> and the  $G$  values given above, a rate constant of  $k(\text{propagation}) = 8.5 \text{ s}^{-1}$  can be calculated for the rate-limiting step. The present results do not allow us to assign this to one distinct elementary step: Elimination of  $\text{H}_2\text{S}$  or  $\text{HS}^\bullet$  (reactions 10 or 11) must compete with the reverse of reaction 8 (reaction 9;  $k_9 \geq 10^8 \text{ s}^{-1}$ ).<sup>15</sup> Thus the  $\text{H}_2\text{S}$  ( $\text{HS}^\bullet$ ) elimination occurs from the quasi-equilibrium (8)/(9) which itself is connected with another quasi-equilibrium (equilibrium (4)/(5)), the equilibrium between the free thyl radical **1** and its three-electron-bonded ring-closed<sup>16</sup> isomer **2**. In the equilibrium between the free thyl radical **1** and its three-electron-bonded ring-closed<sup>16</sup> isomer **2** (equilibrium (14)/(15)),<sup>17</sup> it is to be expected that it is the free thyl radical **1** rather than the ring-closed isomer **2** which undergoes the intramolecular H-abstraction reaction.

(15)  $\alpha$ -Hydroxyalkyl radicals react with DTT in their bimolecular reaction with  $k \geq 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and we estimate that the intramolecular rate constant  $k_9$  should not be lower than  $10^8 \text{ s}^{-1}$ .

(16) For three-electron bonded systems in sulfur free-radical chemistry see ref 7 and: Asmus, K.-D. *Acc. Chem. Res.* 1979, 12, 436. In contrast to the thyl radical derived from 2-mercaptoethanol ( $\text{HOCH}_2\text{CH}_2\text{S}^\bullet$ ) which does not readily reduce tetranitromethane, the DTT radical at pH 4 is rapidly ( $k = 2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) oxidized which is an indication that the reducing three-electron-bonded species **2** must predominate.

(17) The rate constant  $k_{14}$  has been measured by monitoring the buildup of **2** ( $\epsilon(380 \text{ nm}) = 430 \pm 20$ ) at relatively high DTT concentration ( $10^{-3} \text{ M}$ ) and at pH 4 and was found to be  $1.5 \times 10^6 \text{ s}^{-1}$ . Under these conditions reaction 1 is much faster ( $k_1[\text{DTT}] = 2 \times 10^7 \text{ s}^{-1}$ ). A value for  $k_3$  is not yet available, but it is reasonable to assume that it is much lower than  $k_4$  (cf. equilibria between disulphides and thyl radicals: Bonifacic, M.; Asmus, K.-D. *J. Phys. Chem.* 1984, 88, 6286.) Radical **2** has been presented as a three-electron-bonded species, but it cannot yet be excluded that the H atom resides on one of the sulfur atoms.

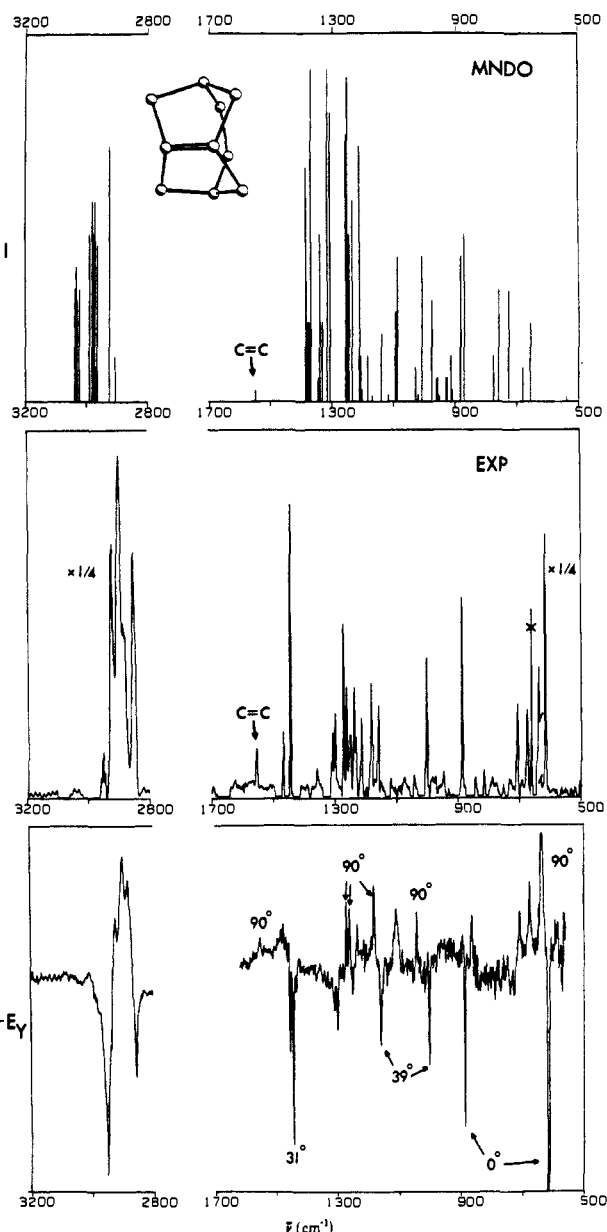
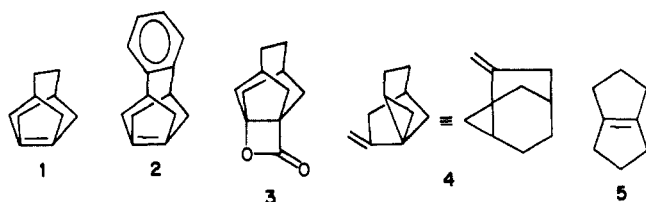
## A Doubly Pyramidalized Olefin: Matrix Isolation Spectroscopy of Tricyclo[3.3.2.0<sup>3,7</sup>]dec-3(7)-ene

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Strong distortions of the C=C double bond from planarity should lead to olefins with unusual properties. Considerable attention has been paid to twisting distortions<sup>2</sup> (e.g., adamantene<sup>3</sup>), relatively less to pure pyramidalization.<sup>4</sup> Tricyclo[3.3.2.0<sup>3,7</sup>]dec-3(7)-ene (**1**)<sup>5</sup> and its benzo derivative **2**<sup>6</sup> have both been



**Figure 1.** IR spectra of **1**: (top) calculated (MNDO, correction factor 0.915); (center and bottom) measured in argon matrix at 10 K ( $\text{CO}_2$  absorption crossed out). The center spectrum was obtained as a difference of spectra recorded before and after photodestruction of **1** at 248 nm. The bottom spectrum is a difference of spectra polarized parallel ( $E_z$ ) and perpendicular ( $E_y$ ) to the electric vector direction of the polarized 248-nm laser light after partial photodestruction of **1** (see text).

generated pyrolytically and trapped chemically. The recent preparation of  $\beta$ -lactone **3** as a precursor for **1**<sup>5</sup> has now permitted the direct observation of this olefin.

Flow pyrolysis ( $450\text{--}650^\circ\text{C}$ ) of **3**, either neat or diluted with excess argon, and deposition onto a 10 K window yielded  $\text{CO}_2$  and a material to which we assign structure **1**. Also detected were

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**Table I.** Vibrations of **1** and Their IR Polarizations<sup>a</sup>

$\nu, \text{cm}^{-1}$		$K$	$\phi_{\text{C}=\text{C}}^b$
Raman	IR		
619	619	0.17	0°
	640	0.36	90°
	889	0.19	0°
	1004	0.27	39 ± 7°
	1161	0.27	39 ± 7°
1265	1184	0.38	90°
	1264	0.39	90°
	1274	0.38	90°
1358	1359	0.36	90°
	1446	0.24	31 ± 6°
1557 <sup>c</sup>	1557	0.37	90°
	2856	0.29	44 ± 7°
	2904	0.36	90°
	2953	0.31	49 ± 7°

<sup>a</sup> Argon matrix, 12 K. <sup>b</sup> Absolute value of the angle between the IR transition moment and the  $\pi\pi^*$  polarization direction. <sup>c</sup> Assigned as the C=C stretch. Calculated frequency, 1546  $\text{cm}^{-1}$  (MNDO  $\times$  0.915), calculated  $\phi_{\text{C}=\text{C}} = 90^\circ$ .

unreacted **3** and, particularly at the higher temperatures, a stable product to which we assign the structure **4**.<sup>7</sup> The evidence for structure **1** is (i) a 1557- $\text{cm}^{-1}$  band in the C=C stretching region, relatively weak in the IR (Figure 1), but the strongest of all the Raman bands. The shift relative to **5** (1685  $\text{cm}^{-1}$ ) is compatible with strong double pyramidalization of **1**. (ii) A broad UV band peaking at 245 ± 15 nm, compatible with the expected lowering of the  $\pi\pi^*$  excitation energy. Irradiation at 248 nm bleaches both the UV and the IR bands associated with **1** and increases the IR peaks of **4**; no additional products are detected. (iii) Above ~165 K in the neat sample, which is quite rigid, and already above ~40 K in the much less viscous argon-matrix-isolated sample, the IR bands of **1** gradually disappear and those of the known<sup>5</sup> 2 + 2 dimer of **1** grow; a GC comparison with an authentic sample (SE-30 column) confirms that the dimer is the chief product formed on warm-up.

A partially aligned sample of matrix-isolated **1** resulted by photoselection upon irradiation with linearly polarized 248-nm light (KrF laser) in ~70% conversion to **4**. The IR dichroic ratios,  $d_i$ , were converted to the orientation factors [ $K_i = \langle \cos^2 i \rangle = d_i / (d_i + 2)$ ,  $i$  is the angle between the  $i$ th transition moment direction and the laboratory axis  $Z$  defined by the electric vector direction of the 248 nm light; the angular brackets indicate averaging over the molecular assembly].<sup>8,9</sup> The  $K_i$  values fall into three categories, separated by margins far in excess of the experimental error (about ±0.03): (i)  $K = 0.17$ –0.19, (ii)  $K = 0.36$ –0.39, (iii)  $0.24 < K < 0.31$  (Table I). Assuming the 248-nm absorption to be polarized along the C=C axis  $x$ , we must have  $K_x < K_y = K_z$ . Since  $\sum_i K_i = 1$ , groups i and ii belong to mutually perpendicular transitions and are within experimental error,  $K_x = 0.20$ ,  $K_y = K_z = 0.40$ .

Since in group iii we observe five lines with  $K_i$  values very different from both 0.20 and 0.40, these are not polarized along  $x$ ,  $y$ , or  $z$ . The absolute values of the angles  $\phi_{\text{C}=\text{C}}$  between the  $x$  axis (C=C) and the IR transition moment directions were obtained from the IR dichroic ratios and the above  $K_x$  and  $K_y$  values by standard procedures<sup>8-10</sup> (Table I). Both the experimental and the calculated polarization of the C=C stretching vibration are perpendicular to the C=C bond, as expected for a doubly pyramidal olefin. Molecular symmetry must be lower than  $C_{2v}$ , and  $C_2$  is the most likely candidate that still preserves orthogonality

among many of the transition moments. This is also the symmetry that was obtained from calculations. The calculated pyramidalization angle at the doubly bonded carbons was 47.8° (MM2), 43.5° (MNDO), and 40.6° (STO-3G), close to the tetrahedral value of 54.7°.

After scaling, the MNDO calculation reproduced very well the 1557- $\text{cm}^{-1}$  frequency of the C=C stretch in **1**. A value of 1546  $\text{cm}^{-1}$  was obtained with a multiplicative correction factor of 0.915, which fits the MNDO calculated frequencies for ethylene and tetramethylethylene to experiment. The MNDO heat of hydrogenation is 47 kcal/mol more negative than the MNDO value for **5**, suggestive of a very highly strained C=C bond.

In conclusion, the first highly reactive representative of a class of doubly pyramidalized olefins has now been directly observed. It has an unusually low-frequency C=C stretching vibration and a low-energy  $\pi\pi^*$  excited state.

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### Synthesis and Characterization of High-Valent Oxo-Olefin and Oxo-Carbonyl Complexes. Crystal and Molecular Structure of $\text{W}(\text{O})\text{Cl}_2(\text{CH}_2=\text{CH}_2)(\text{PMePh}_2)_2$

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Transition-metal oxide compounds catalyze or perform a number of reactions of olefins, including oxidation, polymerization, and metathesis.<sup>2</sup> The active sites for most of these processes are thought to contain terminal oxo ligands. Olefin binding to the metal center has often been suggested as an important step in these reactions but has not as yet been directly observed.<sup>3-5</sup> For example, olefin complexes have been proposed in osmium tetraoxide oxidations,<sup>3</sup> in epoxidations by cytochrome P-450 enzymes,<sup>4</sup> and in tungsten-catalyzed metathesis reactions.<sup>5</sup> We wish to report the first examples of metal complexes containing both simple olefin and terminal oxo ligands. The only previous example of an oxo-olefin compound is an adduct of a very unusual olefin, tetracyanoethylene:  $\text{Mo}(\text{O})[\text{C}_2(\text{CN})_4](\text{S}_2\text{CNR}_2)_2$ .<sup>6</sup> We have also isolated the first carbonyl-terminal oxo complex.<sup>7</sup> The properties of these novel compounds indicate that  $\pi$ -back-bonding can be

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