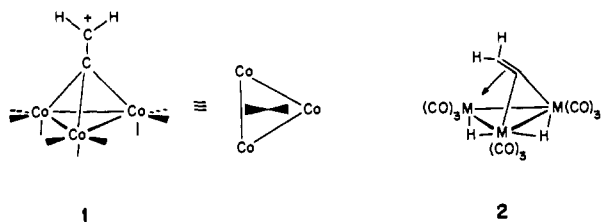


## The Possibility of a Noncentered Structure for $(\text{CO})_9\text{Co}_3\text{CCR}_2^+$

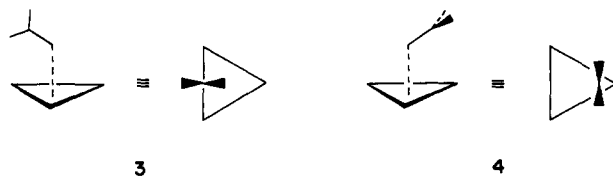
Sir:

There is an interesting and stable set of salts of carbonium ion metal cluster complexes, exemplified by the parent compound  $(\text{CO})_9\text{Co}_3\text{CCH}_2^+$ , **1**.<sup>1</sup> No crystallographic or other direct structural study of these compounds is as yet available.<sup>2</sup> If one were to reason by analogy with the many known  $(\text{CO})_9\text{Co}_3\text{CR}$  structures,<sup>3</sup> one would assume an upright positioning of the CC bond above the center of the tricobalt triangle. The resultant sixfold barrier to  $\text{L}_9\text{Co}_3\text{C}-\text{CH}_2^+$  rotation should be small. This is consistent with the room-temperature NMR spectrum of these complexes.<sup>1,4</sup> The IR band contours of the carbonium ion resemble those of the precursor alcohol,<sup>5</sup> an argument for assigning the same framework symmetry to the two species.

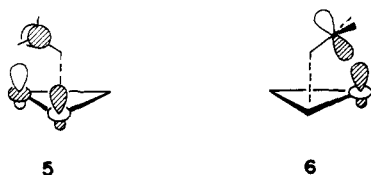


There remains, however, the possibility that the  $\text{CCH}_2$  unit does not stand upright over the center of the ring. One is led to this line of reasoning by the structure of one of the products of the reaction of ethylene with  $\text{M}_3(\text{CO})_{12}$ ,  $\text{M} = \text{Ru}, \text{Os}$ .<sup>6</sup> In this molecule, **2**, two hydrogens have been stripped from the ethylene, yet retained in the cluster. Now  $(\text{CO})_9\text{Co}_3\text{CCH}_2^+$  is in a sense isoelectronic with **2**, if the two bridging hydrogens are counted as protonic. Still closer to the Co cluster is  $(\text{CO})_9\text{Os}_3\text{H}_3\text{CCH}_2^+$ .<sup>7</sup> This last molecule, as judged by NMR evidence, and **2** on the basis of its crystal structure, has the ethylidene  $\sigma$  bonded to two metal atoms,  $\pi$  bonded to the other, in a very unsymmetrical geometry.

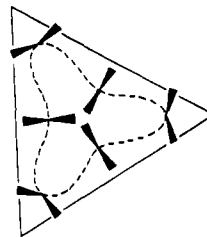
Indeed we find a deformation away from the "upright" position in an extended Hückel calculation on **1**.<sup>8</sup> The potential surface is complicated, for the  $\text{CH}_2$  rotation is coupled with bending of the CC axis away from the central perpendicular to the  $\text{Co}_3$  plane. The preferred orientations are **3**, when the  $\text{CH}_2$  is moving toward a bond center, and **4**, when it is moving toward a unique metal atom.



These preferences may be traced to interaction between the  $-\text{CH}_2$  p orbital and an  $e$  type occupied frontier orbital of the cluster.<sup>8</sup> This degenerate orbital is composed mainly of metal  $z^2$  and has an antisymmetric and a symmetric component. When the  $\text{CH}_2$  group bends toward a Co-Co bond midpoint, the better overlap is with the antisymmetric component, **5**, while when a metal atom is approached the best overlap is attained, in **6**, with the symmetric component. In each case the alternative orientation of the methylene group leads to a poorer interaction.



Our calculations assign the lowest energy to a structure in which the methylene tilts toward a unique metal atom, **4** or **6**, the same deformation as is observed in the cited analogous structures.<sup>6,7</sup> Furthermore, the theory indicates an intricate and specific circumambulation pathway, sketched schematically in **7**.<sup>9</sup> The centered upright structure is avoided.<sup>10</sup>



7

**Acknowledgments.** We are grateful to J. Lewis, B. F. G. Johnson, D. Seyferth, and B. H. Robinson for discussions and the National Science Foundation for its support of this research.

### References and Notes

- (1) For a review see D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976).
- (2) A crystal structure of a salt of **1** is in progress: B. H. Robinson, private communication.
- (3) See B. R. Penfold and B. H. Robinson, *Acc. Chem. Res.*, **6**, 73 (1973), for some leading references.
- (4) D. Seyferth, G. H. Williams, and J. E. Hallgren, *J. Am. Chem. Soc.*, **95**, 266 (1973); D. Seyferth, G. H. Williams and D. D. Traficante, *ibid.*, **96**, 604 (1974).
- (5) D. Seyferth, private communication.
- (6) A. J. Deeming and M. Underhill, *J. Organomet. Chem.*, **42**, C60 (1972); *J. Chem. Soc., Chem. Commun.*, 277 (1973); *J. Chem. Soc., Dalton Trans.*, 1415 (1974).
- (7) A. J. Deeming, S. Hasso, M. Underhill, A. J. Canty, B. F. G. Johnson, W. G. Jackson, J. Lewis, and T. W. Matheson, *J. Chem. Soc., Chem. Commun.*, 807 (1974).
- (8) Details of the calculations, which form part of a general analysis of  $\text{L}_9\text{M}_3$ -(ligand) complexes, will be given in the full publication.
- (9) The computed barrier of 16 kcal/mol is too high, but we have not yet allowed complete relaxation of the molecular framework along the rearrangement path.
- (10) The centered structure is a forbidden transition state, in the sense of R. E. Stanton and J. W. McIver, Jr., *J. Am. Chem. Soc.*, **97**, 3632 (1975).

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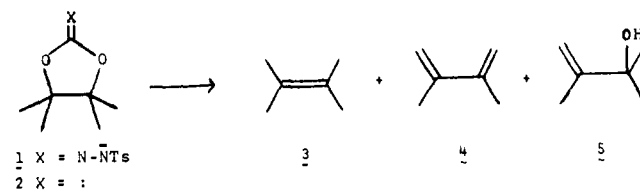
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





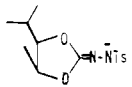
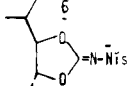
### Pyrolysis of the Carbonate Tosylhydrazone Salts Derived from erythro- and threo-4-Methylpentane-2,3-diol

Sir:

We have reported<sup>1</sup> that pyrolysis of the carbonate tosylhydrazone (CTH) salt derived from pinacol (**1**) gives, in addition to tetramethylethylene (**3**), 2,3-dimethylbutadiene (**4**) and 2,3-dimethylbuten-3-ol (**5**).<sup>2</sup> The formation of **4** and **5** is easily rationalized by mechanisms involving a diradical, produced by homolytic cleavage of one C-O bond in the 2-carbenal, 1,3-dioxolane (**2**) that is presumed to be generated initially by



**Table I.** Percentage Composition<sup>a</sup> of the Volatile Products<sup>b</sup> Trapped in the Pyrolysis of the CTH Salts Derived from *erythro*- and *threo*-4-Methylpentane-2,3-diol

	8	9	10	11	12	13
						
						
						
						
						
						
	31.6	25.7	27.4	8.5	3.4	3.4
	72.0	15.1	4.9	4.9	1.5	1.5

<sup>a</sup> Determined by GLC. See note 9. <sup>b</sup> Products are shown in order of elution.

pyrolysis of **1**.<sup>3</sup> The olefin **3** might be formed from the same diradical, or, alternatively, it could be produced by a concerted [ $\sigma 2_s + \sigma 2_s + \omega 2_s$ ] linear cheletropic process,<sup>4</sup> which is orbital symmetry allowed from the lowest singlet state of **2**.<sup>5</sup>

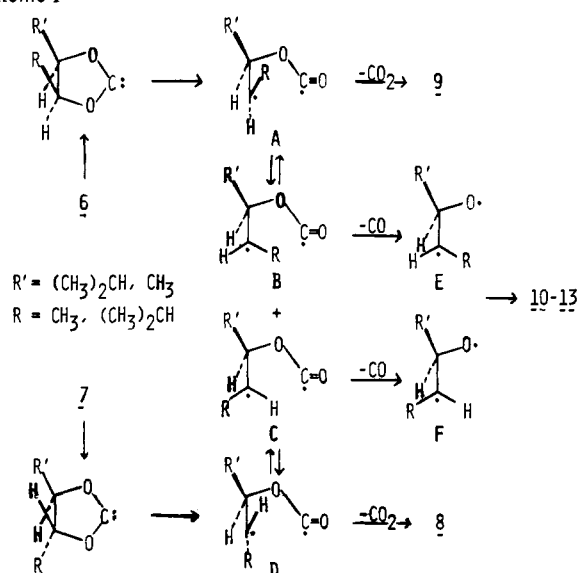
In order to test whether olefins are formed by stepwise or concerted C-O bond breaking in CTH salt pyrolyses, we have examined the products formed from thermal decomposition of the CTH salts derived from *threo*- and *erythro*-4-methylpentane-2,3-diol.<sup>6</sup> We report herein results that are indicative of a diradical precursor of the olefins formed and that provide evidence of the importance of conformation in the partitioning of the diradical into products.

The *threo* and *erythro* diols were converted into the CTH derivatives by reaction with "phosgene immonium chloride", followed by treatment of the cyclic immonium salt intermediates with tosylhydrazine.<sup>1,7</sup> From this reaction sequence pure *cis* (mp 127-128 °C) and *trans* (mp 155-157 °C) CTH's<sup>8</sup> could be obtained in 45-50% yield. The CTH's were transformed into the sodium salts by reaction with sodium hydride in THF. The salts were dried in a vacuum desiccator overnight and then pyrolyzed under vacuum, as described previously.<sup>1</sup> The volatile products trapped were separated by GLC<sup>9</sup> and identified by comparison of their NMR spectra and GLC retention times with those of authentic samples. The products and the relative amount of each obtained from the *cis* (**6**) and *trans* (**7**) salt are shown in Table I.

The products formed from pyrolysis of **6** and **7** can be rationalized on the basis of one-bond cleavage in carbenadioxolane intermediates, as illustrated in Scheme I. It is clear from the data in Table I that olefin formation is nonstereospecific; in fact, *trans* olefin **8** is formed in higher yield from the *cis* salt **6** than is *cis* olefin **9**. There is considerably less leakage from the *trans* salt **7** to the *cis* olefin **8**. The *cis* salt **6** also produces substantially larger amounts of oxygen-containing products than does the *trans* salt **7**. As discussed previously,<sup>1</sup> it seems likely that the oxygen-containing products arise primarily from conformations resembling **B** and **C**, where some C-C bond rotation has occurred in the initially formed diradicals, making direct formation of planar olefins by CO<sub>2</sub> loss impossible.<sup>10</sup> This hypothesis allows correlation of the fact that **6** gives a higher percentage than **7** of olefin with inverted stereochemistry with the observation that larger amounts of oxygen-containing products also are formed from **6**. Both results may thus be viewed as indicating that conformations resembling **A** are depopulated more rapidly by C-C bond rotation than those resembling **D**.

Another interesting difference between the products formed from the *cis* and *trans* salts is the ratio of *trans* epoxide **10** to *cis* epoxide **11**. The ratio of **10/11** is >3 in the pyrolysis of **6**,

Scheme I



while it is only 1.0 when **7** is decomposed thermally. The fact that the **10/11** ratio is higher in the pyrolysis of **6** than **7** is quite surprising. It contrasts with the finding that addition of <sup>31</sup>P oxygen atoms to *trans*-2-butene results in the formation of a higher ratio of *trans* to *cis* epoxide than does the addition to *cis*-2-butene.<sup>11</sup> Although similar diradical intermediates are postulated as the epoxide precursors in both reactions, the different modes by which these intermediates are generated could easily account for this difference in their behavior.<sup>12</sup>

Two similarities between the products obtained from pyrolysis of **6** and **7** also merit comment. First, within experimental accuracy the ratio of the two ketones, **12** and **13**, formed from each salt is unity. This shows that the C-O bond broken in the presumed carbenadioxolane intermediate does not depend on whether the carbon bears a methyl or isopropyl group. Second, and certainly more surprising, dienes and allylic alcohols analogous to **4** and **5** are not formed (<1%) in the pyrolysis of either **6** or **7**. Presumably, this reflects the availability of conformations like **C** and **F** to the diradicals generated from **6** and **7**. In these conformations hydrogen abstraction from **R**, which, prior to decarbonylation, would lead ultimately to diene formation and, subsequent to decarbonylation, would produce allylic alcohols, is impossible. Such conformations are, of course, unavailable to the diradical intermediates formed from the CTH salt of a tertiary diol like pinacol.<sup>13</sup>

In summary, the products obtained from pyrolysis of **6** and **7** appear to be best rationalized as being formed from partially equilibrated diradicals, generated by one-bond cleavage in a putative carbenadioxolane intermediate. If a carbenadioxolane is, indeed, an intermediate in CTH salt pyrolysis, it certainly does not undergo the concerted [ $\sigma 2_s + \sigma 2_s + \omega 2_s$ ] loss of CO<sub>2</sub> that apparently occurs in other reactions where carbenadioxolanes have been proposed as intermediates.<sup>14</sup> In fact, acyclic dialkoxy carbenes, formed from CTH salt pyrolysis,<sup>15</sup> also exhibit different chemistry than those produced by thermal decomposition of norbornadione ketals.<sup>16</sup> We are investigating the intriguing possibility that different modes of generation may lead to population of different electronic states of dialkoxy carbenes.<sup>17</sup>

**Acknowledgment.** We thank the National Science Foundation and the Alfred P. Sloan Foundation for partial support of this work.

#### References and Notes

- W. T. Borden, P. W. Concannon, and D. I. Phillips, *Tetrahedron Lett.*, 3161 (1973).

- (2) Subsequently we have found that the product mixture also contains a very small amount of 2,3-dimethyl-1-butene.
- (3) Pyrolysis of tosylhydrazone salts under aprotic conditions generally leads to carbenes. See W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn in "Carbenes", Vol. 1, M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N.Y., 1973, p 1, for numerous examples.
- (4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **11**, 761 (1969).
- (5) A. M. Foster and W. C. Agosta, *J. Am. Chem. Soc.*, **95**, 609 (1973), have found that olefins are formed with a high degree of stereospecificity in the pyrolysis of  $\gamma$ -lactone tosylhydrazone salts. These authors have suggested that a concerted mechanism for olefin formation competes with a diradical pathway, which leads to the other products that are formed.
- (6) These diols have been used previously to establish the stereospecificity of olefin formation in the reactions of the derived thionocarbonates with Ni(0): M. F. Semmelhack and R. D. Stauffer, *Tetrahedron Lett.*, 2667 (1973). We thank Professor Semmelhack for sending us his procedure for preparing the diols.
- (7) B. Le Clef, J. Mommaerts, B. Stelander, and H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **12**, 404 (1973), have reported that the cyclic ammonium salts formed from secondary glycols undergo  $S_N2$  ring opening by chloride ion to give chlorocarbonates. We minimized this undesired process by limiting the time of the initial reaction to 30 min in refluxing  $CH_2Cl_2$ . Small resonances attributable to chlorocarbonate were observed in the NMR spectra of the crude ammonium salts; however, purification of the moisture sensitive salts was not attempted. Instead, the crude salts were allowed to react with tosylhydrazine in a refluxing mixture of tetrahydrofuran and triethylamine, as described previously<sup>1</sup>, and the resulting CTH's were purified by recrystallization.
- (8) Both CTH's gave satisfactory elemental analyses and exhibited spectral data consistent with the assigned structures.
- (9) The products were separated on a 16 ft  $\times$   $\frac{1}{8}$  in column of 8%  $AgNO_3$  on Chromosorb P. Peak areas were corrected for differences in the response of the thermal conductivity detector to the products. A few percent of toluene was also detected among the volatile products that were trapped.
- (10) This hypothesis nicely rationalizes the observation that the CTH salt derived from bicyclo[3.3.0]octane-1,5-diol gives only bicyclo[3.3.0]oct-1(5)-ene on pyrolysis,<sup>1</sup> since in this rigid ring system C-C bond rotation cannot occur.
- (11) R. J. Cvetanovic, *Adv. Photochem.*, **1**, 115 (1963).
- (12) Not only could the diradicals differ in the conformations and spin states initially populated, but the diradicals formed by oxygen atom addition possess sufficiently large quantities of vibrational energy that fragmentation is competitive with epoxide formation.<sup>11</sup>
- (13) It should also be noted that, while the percentage of olefin formed from pyrolysis of 1<sup>1</sup> and 7 is about the same, the percentage of oxygen-containing product obtained from the former CTH salt is much lower than that produced from the latter. This reflects the fact that a substantial portion of the diradicals generated by one-bond cleavage in 2 abstracts hydrogen before decarbonylating, leading, after loss of formic acid, to 4.
- (14) F. W. Eastwood, K. J. Harrington, J. S. Josan, and J. L. Pura, *Tetrahedron Lett.*, 5223 (1970); G. Crank and F. W. Eastwood, *Aust. J. Chem.*, **17**, 1392 (1964); J. S. Josan and F. W. Eastwood, *ibid.*, **21**, 2013 (1968); S. Hanessian, A. Bargiotti, and M. LaRue, *Tetrahedron Lett.*, 737 (1978).
- (15) R. J. Crawford and R. Raap, *Proc. Chem. Soc. (London)*, 370 (1963).
- (16) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1962); R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **10**, 529 (1971).
- (17) Carbene formation by deprotonation of a carbocation intermediate<sup>14</sup> or by norbornadienone ketal pyrolysis<sup>16</sup> is symmetry allowed in the sense that filled orbitals of the reactant correlate directly with those populated in the lowest singlet state of the carbene product. In contrast, linear cheletropic loss of nitrogen from a diazo compound is an orbital symmetry forbidden process. Ab initio calculations on diazomethane suggest that this compound, in fact, decomposes by a nonlinear cheletropic pathway.<sup>18</sup>
- (18) J. Lievin and G. Verhaegen, *Theor. Chim. Acta*, **45**, 269 (1977).

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## Wavelength Dependent Photoprocesses in Acenaphthaquinone

Sir:

Typically, the internal conversion  $S_n \rightsquigarrow S_1$  dominates the upper excited state photophysics of polyatomics in fluid media. Exceptions such as azulene<sup>1</sup> and thioketones<sup>2</sup> are rare and noteworthy since they offer an opportunity to elucidate upper state relaxation schemes. We report herein results showing the wavelength dependence of several photoprocesses involving acenaphthaquinone (ANQ).<sup>3</sup> These observations suggest *less*

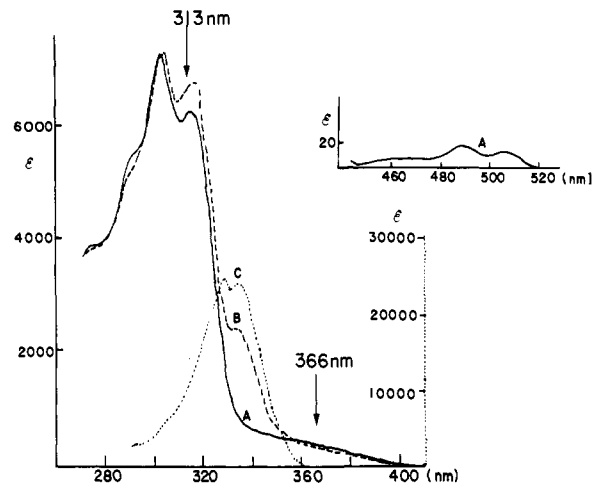


Figure 1. Absorption spectra of acenaphthaquinone in cyclohexane (A) after rigorous purification and (B) before purification, and of (C) 1,8-naphthalic anhydride in benzene (A and B), left-hand scale; C, right-hand scale.

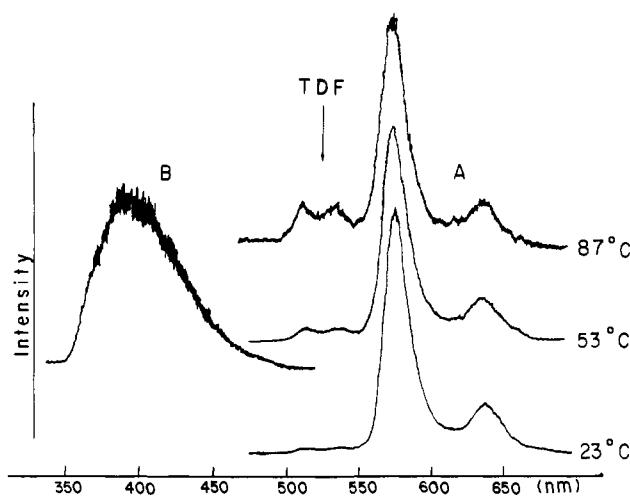


Figure 2. Time-resolved emissions from degassed solutions of  $1.0 \times 10^{-4}$  M acenaphthaquinone in benzene at 25 °C: (A) longer lived emissions recorded with a time delay of 10  $\mu$ s and a sampling gate of 2  $\mu$ s at temperatures indicated; (B) fluorescence from trace 1,8-naphthalic anhydride recorded with a time delay of 0 ns and a sampling gate of 10 ns.

than complete relaxation of an upper excited state in ANQ to the lowest excited states in fluid media.

Absorption spectra data for ANQ are shown in Figure 1. The very weak ( $\epsilon \approx 20$ ) long wavelength absorption near 500 nm is an  $n, \pi^*$  transition,<sup>4</sup> while the more intense absorptions near 300 nm are  $\pi, \pi^*$  transitions. The weaker ( $\epsilon \approx 400$ ) broad shoulder,  $< 400$  nm, may be a second  $n, \pi^*$  transition.<sup>4a</sup> The peak previously reported<sup>5</sup> at 338 nm (Figure 1B) is due to 1,8-naphthalic anhydride (NA) (Figure 1C). This troublesome impurity, arising from facile photooxidation of ANQ<sup>6</sup> (discussed below), has a strong ( $\Phi_f = 0.26$ ) (Figure 2B) but short-lived ( $\tau_f < 10$  ns) fluorescence. We estimate that observable impurity fluorescence is detectable at an NA level of  $\geq 0.05\%$  under our experiments.

Nitrogen laser excitation (337 nm, 10 ns pulse) of degassed and sealed samples of purified<sup>3</sup> ANQ in benzene provided the time-resolved<sup>7</sup> emissions in Figure 2. The spectrum of the fast decaying ( $\tau < 10$  ns), short wavelength emission is fluorescence from low levels of NA. The longer lived emissions ( $\tau \approx \mu$ s) are assigned to mixed thermal delayed fluorescence (TDF)<sup>8</sup> and phosphorescence from the  $n, \pi^* S_1$  and  $T_1$  states of ANQ. From the temperature dependence of  $\Phi_{TDF}/\Phi_p$  (Figure 2A),  $\Delta E_{S_1-T_1} = 1780 \pm 120 \text{ cm}^{-1}$ , which is consistent with the  $n, \pi^*$