

cP and fell off at higher viscosities. A plot of $\log k^0$ vs. $\log D$ had a slope of 0.7 over the whole range of η .

Although the classical et reaction theories, e.g., that of Marcus,¹⁰ do not suggest a solvent viscosity dependence for outer-shell et, more recent theoretical treatments¹⁻⁴ emphasize the role of solvent dynamics. For example, Calef and Wolynes¹ stress the importance of the dielectric relaxation and thermal reorientation times of the solvent (which depend upon viscosity) in determining the pre-exponential factor in the rate expression. Rotational reorientation dynamics of the molecule undergoing the et reaction may also be important.

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Registry No. $\text{Fe}(\text{CN})_6^{3-}$, 13408-62-3; $\text{Fe}(\text{CN})_6^{4-}$, 13408-63-4; K_2SO_4 , 7778-80-5; TBABF_4 , 429-42-5; dextrose, 50-99-7; ferrocene, 102-54-5; ferrocenium, 12125-80-3; sucrose, 57-50-1.

(10) Marcus, R. A. *J. Chem. Phys.* 1965, 43, 679.

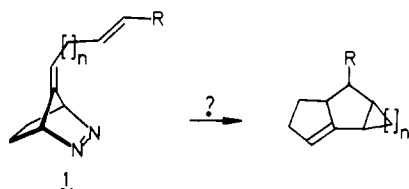
Evidence for Hydrogen Atom Abstraction and Loss of Diylophile Stereochemistry in an Intramolecular 1,3-Diyl Trapping Reaction

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Of the many unexplored questions concerning the factors that govern the outcome of intramolecular 1,3-diyl trapping reactions, one that is very easy to formulate focuses upon the course of the reaction as a function of the length of the tether that links the diyl and diylophile. Until now, the tether length has been restricted to cases where $n = 3$ (see 1), and in all but one recorded instance, linearly fused cycloadducts (viz., those with a tricyclo-[6.3.0.0^{2,6}]undecane skeleton) have corresponded to the major products.¹ Is this a general result? That is, will linearly fused products be formed regardless of the length of the tether? In this manuscript, we examine the chemistry of the diyl derived from 1 where $n = 2$ and $R = \text{CO}_2\text{CH}_3$.



The diazene required to initiate this investigation was prepared from 4-hydroxybutanal, cyclopentadiene, and bis[(2,2,2-trichloroethoxy)carbonyl] azodicarboxylate by following a sequence analogous to that which we have published previously.²

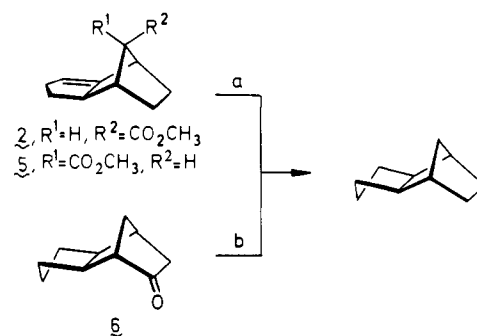
[†]UCSB.

[‡]WVU.

(1) Little, R. D.; Carroll, G. L.; Petersen, J. L. *J. Am. Chem. Soc.* 1983, 105, 928.

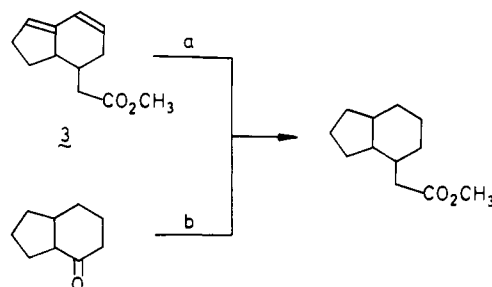
(2) See, for example: (a) Little, R. D.; Carroll, G. L. *J. Org. Chem.* 1979, 44, 4720. (b) Little, R. D.; Muller, G. W. *J. Am. Chem. Soc.* 1981, 103, 2744. (c) Stone, K. J.; Little, R. D. *J. Org. Chem.* 1984, 49, 1849. (d) Little, R. D.; Muller, G. W.; Venegas, M. G.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stone, K. J. *Tetrahedron* 1981, 37, 4371.

Scheme I^a



^a (a) (1) KOH, MeOH; (2) H_2 , 10% Pd/C; (3) ref 3. (b) (1) $\text{HSCH}_2\text{CH}_2\text{SH}$, BF_3 ; (2) Raney nickel.

Scheme II^a



^a (a) H_2 , 10% Pd/C; (b) $[(\text{MeO})_2\text{POCHCO}_2\text{CH}_3] \text{Na}$, DME, then $\text{BH}_3\text{-THF}$ and MeOH.

A 5 mM solution of 1 dissolved in THF was heated at reflux until the starting material disappeared as evidenced by TLC. After removal of the solvent, careful analysis of the reaction mixture by capillary column GC and 300-MHz ¹H NMR (PMR) revealed the presence of four components 2-5 (83% isolated yield), formed in a ratio of 16:5:1.5:1. The two major products 2 and 3 were separated from each other and the remaining materials. Mass spectral and elemental analysis indicated that they were isomeric, each having a structural formulation corresponding to $\text{C}_{12}\text{H}_{16}\text{O}_2$. Catalytic hydrogenation of the major product 2 followed by inspection of the fully decoupled ¹³C NMR spectrum of the resulting product revealed only 8 rather than 12 lines anticipated for a linearly fused product, i.e., one with a tricyclo[6.2.0.0^{2,6}]decane skeleton. This result suggests either that several of the resonances of a linearly fused cycloadduct are accidentally degenerate or that the molecule is not linearly fused and instead possesses an element of symmetry.

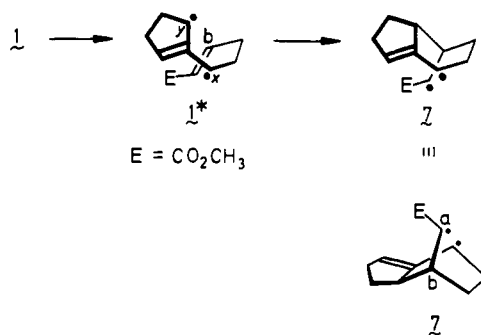
The gross structural features of this material were determined by following the sequence outlined in Scheme I. That is, 2 was saponified, the carbon-carbon π bond was reduced, and the carboxylic acid unit was removed using a Barton decarboxylation sequence.³ The resulting hydrocarbon proved to be identical with that derived from the commercially available 8-ketotricyclo[5.2.1.0^{2,6}]decane (6)⁴ after removal of the carbonyl. The stereochemical disposition of the ester unit was established unambiguously through a single-crystal X-ray structural analysis of the carboxylic acid derived from 2.⁵ As illustrated, the carboxylic acid unit is oriented anti to the endocyclic five-membered ring. In other words, the stereochemistry about the diylophile π bond has been lost. Such a result is unprecedented; all previous intramolecular diyl trapping reactions wherein diylophile stereochemistry has been an issue have proceeded stereospecifically and

(3) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* 1983, 939.

(4) This material is available from the Aldrich Chemical Co.

(5) (a) To be certain that epimerization did not occur during the saponification of ester 2, the carboxylic acid was reesterified and was shown to be identical with 2. (b) Full X-ray data is available as supplementary material.

Scheme III



have maintained the diylophile stereochemistry.^{2b,d}

In a similar fashion, it was determined that minor product **5** also possesses the same ring system and that it is isomeric with **2** about the ester-bearing carbon. Finally, the minor product **4** was subjected to the same sequence and the resulting hydrocarbon was compared with and seen to be different from that derived from **6**. However, comparison with the hydrocarbon derived from catalytic hydrogenation of *endo*-dicyclopentadiene established that **4** possesses the same basic skeleton as **5** but differs in that the five-membered ring is endocyclic in compound **4**.

Inspection of the ¹H NMR spectrum of the second major component **3** indicates the presence of three vinyl protons corresponding to the four sp² hybridized carbons which are evident in the CMR spectrum of **3**. Furthermore, the UV spectrum shows a maximum at 235 nm with an extinction coefficient of ca. 8000. Clearly, this material contains a conjugated diene unit. The nature of the carbon skeleton, but not the stereochemistry, at the relevant stereocenters in **3** was determined unambiguously by following the sequence of reactions outlined in Scheme II. In particular, both **3** and the previously characterized bicyclo[4.3.0]nonan-2-one⁶ are convertible to the same materials.

The chemistry of the diyl derived from diazene **1** differs markedly from that of any other we have examined. The nature of the products, especially the presence of stereoisomers and product **3**, suggests that they are formed in a nonconcerted reaction. In fact, their formation can most simply be rationalized by applying some of the ground rules that are typically associated with the closure of a monoradical onto an alkene;⁷ that is, given the option of closing between C_y and C_b to form a six-membered ring (6-*exo*,*trig* closure) or between C_x and C_b to form the significantly more strained four-membered ring (4-*exo*,*trig* closure), the literature clearly indicates that the former is kinetically preferred. Furthermore, studies of the equilibrium between the 4-pentenyl radical and cyclobutylcarbinyl show that, while the reaction is reversible, the equilibrium lies far to the side of the open form.⁷ Since no linearly fused product was identified, one is forced to conclude either that, in this instance too, a 4-*exo*,*trig* closure does not occur or that it is reversible and eventually leads to **7**, the diyl derived from **1*** by 6-*exo*,*trig* closure. Carbon-carbon bond formation between the two odd-electron centers in **7** (Scheme III) with concomitant rotation about the C_a-C_b bond leads to **2** and without rotation to **4** and **5**, while an *unprecedented* (in our experience with diyl chemistry) hydrogen atom abstraction leads to diene **3**.

We are continuing our efforts to determine the fundamental factors that govern the course of the diyl trapping reaction and to apply the results of those investigations to the construction of structurally interesting and potentially useful natural products.

Acknowledgment. This investigation was supported by PHS Grant CA 21144, awarded by the National Cancer Institute.

(6) (a) Weisbuch, F. C. R. *Seances Acad. Sci. Paris, Ser. C* **1966**, 1234. (b) Le Goffic, Y. *Bull. Soc. Chim. Fr.* **1965**, 2250. (c) Dana, G.; LoCicero, B.; Weisbuch, F. *J. Org. Chem.* **1981**, *46*, 914.

(7) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 4.

DHHS. We are grateful for their continued support of our research. Partial support from the Alfred P. Sloan Foundation in the form of a fellowship to R.D.L. is also gratefully acknowledged.

Supplementary Material Available: Full X-ray data and perspective views of the molecular structure for C₁₁H₁₄O₂ (16 pages). Ordering information is given on any current masthead page.

Tetranuclear Carbido-tungsten and Nitridomolybdenum Clusters Supported by Alkoxide Ligands: W₄(C)(O-*i*-Pr)₁₂(NMe) and Mo₄(N)₂(O-*i*-Pr)₁₂

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We report here our discovery of the first examples of carbido and nitrido clusters of tungsten and molybdenum supported by alkoxide ligands.¹

The reaction between W₂(NMe₂)₆(M≡M) and *i*-PrOH (>>6 equiv) in hexane at room temperature has been shown to yield W₄(H)₂(O-*i*-Pr)₁₄² by way of an intermediate, W₂(O-*i*-Pr)₆(HNMe₂)₂,³ which is the major product at short reaction times (<1 h). However, a persistent impurity in preparations of W₂(O-*i*-Pr)₆(HNMe₂)₂ is a black crystalline compound, W₄(C)(NMe)(O-*i*-Pr)₁₂ (**I**), which is formed in ca. 5-10% yield based on tungsten.⁴ Compound **I** does not react with *i*-PrOH to give W₄(H)₂(O-*i*-Pr)₁₄ and appears to be formed competitively with W₂(O-*i*-Pr)₆(HNMe₂)₂ during the alcoholysis of W₂(NMe₂)₆ since we have been unable to convert pure samples of W₂(O-*i*-Pr)₆(HNMe₂)₂ to **I**. Compound **I** is presumably formed by degradation of a NMe₂ ligand, possibly by way of a (μ-CH₂)NMe ligand as recently noted in reactions of NMe₂ ligands at the W₂⁶⁺ center.⁵ Our formulation of **I** as the carbido cluster W₄(C)(NMe)(O-*i*-Pr)₁₂ is based on elemental analyses, a single-crystal X-ray study, the appearance of the molecular ion cluster in the low-resolution electron impact mass spectrum, and NMR spectroscopy which reveals the presence of 12 different O-*i*-Pr ligands, the NMe group, and the carbido carbon: δ(W₄(C)) 366.8 relative to Me₄Si.⁶ We have not, using natural abundance ¹³C samples with Cr(acac)₃, been able to resolve any of the satellite spectrum which is expected due to coupling to four different ¹⁸³W nuclei (¹⁸³W, *I* = 1/2, natural abundance = 14.5%).

(1) For recent reviews of carbido, nitrido, and alkoxide chemistry, see ref 1a, 1b, and 1c, respectively: (a) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1. Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203. (b) Dehnicke, K.; Strahle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413. Gladfelter, W. L. In "Organometallic Compounds: Synthesis, Structure and Theory"; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1983; p 281. (c) Bradley, D. C.; Mehrota, R. C.; Gaur, P. D. "Metal Alkoxides"; Academic Press: New York, 1978. Mehrota, R. C.; Martin, R. L. *J. Organomet. Chem.* **1982**, *239*, 159.

(2) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Leonelli, J.; Little, D. *J. Am. Chem. Soc.* **1981**, *103*, 779.

(3) Chetcuti, M. J.; Chisholm, M. H.; Huffman, J. C.; Leonelli, J. *J. Am. Chem. Soc.* **1983**, *105*, 292.

(4) Note the use of dry and oxygen-free atmospheres (N₂) and solvents. Pure crystalline samples of **I** were separated from W₂(O-*i*-Pr)₆(HNMe₂)₂ by hand in a Vacuum Atmospheres Dri-Box.

(5) Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 152.

(6) Crystal data (i) for W₄(O-*i*-Pr)₁₂(μ-NMe)(C) at -165 °C: *a* = 19.379 (1) Å, *b* = 12.516 (1) Å, *c* = 11.883 (1) Å, α = 119.37 (6)°, β = 84.98 (5)°, γ = 98.79 (5)°, *Z* = 2, *d*_{calcd} = 1.988 g cm⁻³, and space group *P*1. Final residuals are *R*(*F*) = 0.054 and *R*_w(*F*) = 0.046. (ii) for Mo₄(N)₂(O-*i*-Pr)₁₂ at -160 °C: *a* = 11.338 (3) Å, *b* = 12.568 (3) Å, *c* = 11.348 (3) Å, α = 95.84 (2)°, β = 119.55 (1)°, γ = 67.81 (2)°, *Z* = 1, *d*_{calcd} = 1.437 g cm⁻³, and space group *P*1. Final residuals are *R*(*F*) = 0.019 and *R*_w(*F*) = 0.024.