$[Ph_3PCuH]_6$, a more convenient preparation uses 1 equiv of $NaBH_4$ in THF/H_2O as described by Graham.[5e] Thus after $NaBH_4$ (15 mg, 0.39 mmol) in 1 mL of 1:1 THF/H_2O is allowed to react with $[(\eta\text{-}C_5Me_5)Ru(CO)_2PMe_2Ph]^+[I]^-$ (**2**)[8] (204 mg, 0.37 mmol) in 3 mmol of THF, yellow crystals of **4** (150 mg, 95%) can be isolated.[8] Carefully degassed C_6D_6 solutions of **4** (sealed tube) are stable indefinitely at room temperature. However, at 40 °C, the formyl complex in solution decomposes at varying rates. The following experiment based on the results obtained with complex **3** was undertaken. A C_6D_6 solution of **4** was divided into two NMR tubes—one containing 2 equiv of 9,10-dihydroanthracene and the other one empty—sealed under vacuum and placed in a 40 °C constant-temperature bath. Periodically the samples were removed from the bath and the ^1H NMR spectra recorded. Within 1 h, the sample that did not contain a radical trap had decomposed to a 50:50 mixture of $(\eta\text{-}C_5Me_5)Ru(CO)_2H$ (**5**) and $(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)H$ (**6**). Within several additional hours of heating, the dicarbonyl hydride **5** in this sample was completely converted to **6**. In stark contrast, the sample containing 9,10-dihydroanthracene decomposed to a 50:50 mixture of **5** and **6** only *after 14 days of heating at 40 °C*. An additional day of heating did not substantially change this ratio.

A possible explanation for the results of decomposition of formyl complexes both in the presence of and in the absence of 9,10-dihydroanthracene is presented in Scheme I. We are, therefore, proposing that the neutral formyl complexes do not decompose by the accepted route, i.e., loss of terminal carbon monoxide followed by deinsertion of the formyl carbonyl, but instead by a pathway initiated by cleavage of the carbon-to-hydrogen bond of the formyl group by miscellaneous radicals. Radical scavengers, such as 9,10-dihydroanthracene, greatly reduce the concentration of such radicals and therefore retard the decomposition of the formyl complexes. Further support for lack of carbon monoxide loss in the initial step is that $(\eta\text{-}C_5Me_5)Ru(CO)_2CH_2OH$ decomposes only at a temperature greater than 100 °C.[4] Loss of carbon monoxide is presumed to be the first step in this decomposition.[5d] The intermediate **7** formed in the initial hydrogen atom abstraction could be viewed as an acyl radical similar to that commonly proposed in radical-initiated reactions of aldehydes or, alternatively, as a 19-electron ruthenium complex. We believe that once $(\eta\text{-}C_5Me_5)Ru(CO)_2\cdot$ and $(\eta\text{-}C_5Me_5)Ru(CO)(PMe_2Ph)\cdot$ are formed their reaction with **4** is fast, and 9,10-dihydroanthracene does not effectively intercept these 17-electron species until all the formyl complex is decomposed. The decomposition experiment also indicates that reaction of **5** with PMe_2Ph is probably radical initiated since the rate of this substitution slows drastically in the presence of 9,10-dihydroanthracene.

We believe that the data presented here—(1) variable rates of decomposition of the neutral metal formyl complexes **3** and **4** and (2) stabilization of **4** in solution by radical scavengers—indicate that decomposition takes place via a radical chain process involving cleavage of the carbon-to-hydrogen bond of the formyl group in a kinetic step followed by decomposition of the ensuing acyl radical to a more stable ruthenium radical that is the chain carrier. We are continuing to study this and other aspects of carbon monoxide reduction in model ruthenium complexes.

Acknowledgment. We thank the Eastman Chemicals Division for allowing publication of this work.

Registry No. 1, 86853-54-5; **2**, 88296-33-7; **3**, 88296-34-8; **4**, 88296-35-9; **5**, 82728-97-0; **6**, 88296-36-0; $[Ph_3PCuH]_6$, 33636-93-0; DHA, 613-31-0.

Supplementary Material Available: Experimental details for preparation of $(\eta\text{-}C_5Me_5)Ru(CO)_2(PMe_2Ph)^+I^-$ (**2**) and NMR, IR, and analytical data for **2** and **4** (1 page). Ordering information is given on any current masthead page.

(8) Analytical data for complexes **2** and **4** are satisfactory and are detailed in the supplementary material. An X-ray structure of **4** has been completed: details will be reported later.

Synthesis and Thermal Isomerization of a Cyclobuta[*d*]naphthalenone

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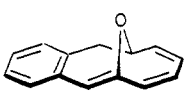
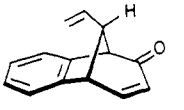
Orbital symmetry constraints serve in an entirely predictable manner to guide many molecules into well-defined thermal and photochemical reaction channels. Effects that may be capable of interfering with this normal kinetic preference have not been systematically investigated, are viewed as subtle, and are not widely appreciated. In the course of another study, we had occasion to prepare the topologically interesting tetracyclic ketone **6**[3] and to examine its thermolysis. An unprecedented, preparatively useful route to benzo fused oxa[10]annulene **7** was uncovered. Of complementary mechanistic significance is the notable involvement of the carbonyl group of **6** in a "symmetry-disallowed" bond reorganization scheme which evidently proceeds at the expense of a Cope rearrangement.

The synthetic protocol (Scheme I) began with selective hydrolysis of diester **1a**[4] (88%) and conversion to crystalline ketone **2** (mp 49–50 °C) by cuprate addition to the acid chloride (88% for two steps).[5] Following ketalization and alteration of the ester oxidation level to give aldehyde **3** (75% overall), the [4.4.4]propellatrienone **4**, mp 55–56 °C, was obtained conventionally (43%). Treatment of **4** with 2 equiv of bromine afforded **5**, which when exposed directly to potassium *tert*-butoxide in dry dimethylformamide (−30 °C, 3 h) furnished **6**, mp 140 °C (55%). The structural assignment to **6**, which was substantiated by X-ray analysis (Figure 1), explicitly defines the striking capacity of enolate anion 5^- for 1,4-elimination. No five-ring product resulting from 1,5-elimination was detected.

The thermolysis of **6** was most conveniently carried out on packed (Carbowax 20M, SE-30, or QF-1) VPC columns in the 130–175 °C range. Under these conditions, **7** and **8** were efficiently produced in an approximate ratio of 1.1:1.0 and separated chromatographically (7% SE-30 on Chromosorb W, 130 °C). Immediate recourse to X-ray methods showed **7** (mp 96 °C) to be an interesting benzo fused oxa[10]annulene derivative (Figure 2). The structural features of **8** (mp 83 °C) were deduced from its IR and NMR spectra.[6]



7



8

The proportion of **7** to **8** remained constant over a wide range of conditions and was invariant to the percent conversion of **6**. A common intermediate is assumed in their formation. While

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(2) (a) The Ohio State University. (b) Authors to whom inquiries concerning the X-ray analyses should be directed at the University of Houston.

(3) The *Chemical Abstracts* name for this substance is 2,2a-dihydro-2,5a-etheno-5a*H*-cyclobuta[*d*]naphthalen-3(1*H*)-one [Merritt, J., private communication].

(4) Paquette, L. A.; Ohkata, K.; Jelich, K.; Kitching, W. *J. Am. Chem. Soc.* **1983**, *105*, 2800.

(5) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1979**, *101*, 6991 and references cited therein.

(6) IR (KBr) (cm^{-1}) 3070 (w), 3000 (w), 1677 (s), 1635 (w); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.48 (dd, J = 9.6 and 6.9 Hz, 1 H), 7.38 (dd, J = 5.1 and 3.3 Hz, 1 H), 7.25 (m, 1 H), 7.15–7.11 (m, 2 H), 5.66 (ddd, J = 17.2, 10.2, and 7.2 Hz, 1 H), 5.51 (dd, J = 9.6 and 1.6 Hz, 1 H), 5.13 (dt, J = 17.2 and 1.2 Hz, 1 H), 5.02 (dd, J = 10.3 and 1.0 Hz, 1 H), 3.78 (br s), 3.60 (d, J = 7.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) (ppm) 197.75 (s), 154.54 (d), 146.78 (s), 137.74 (s), 137.55 (d), 127.42 (d), 127.17 (d), 126.51 (d), 124.00 (d), 123.90 (d), 117.28 (t), 64.85 (d), 63.64 (d), 48.95 (d).

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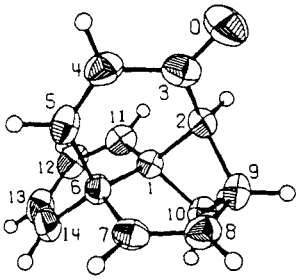


Figure 1. Computer-generated perspective drawing of the final X-ray model of **6**. The thermal ellipsoids are 50% equiprobability envelopes with hydrogens as spheres of arbitrary diameter.

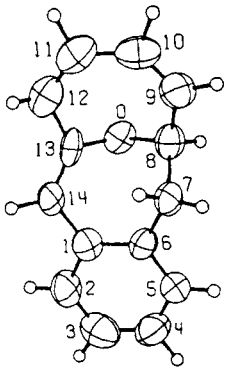
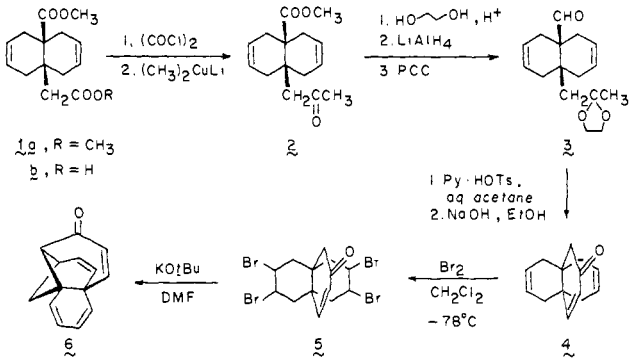


Figure 2. Computer-generated perspective drawing of the final X-ray model of **7**. The thermal ellipsoids are 50% equiprobability envelopes with hydrogens as spheres of arbitrary diameter.

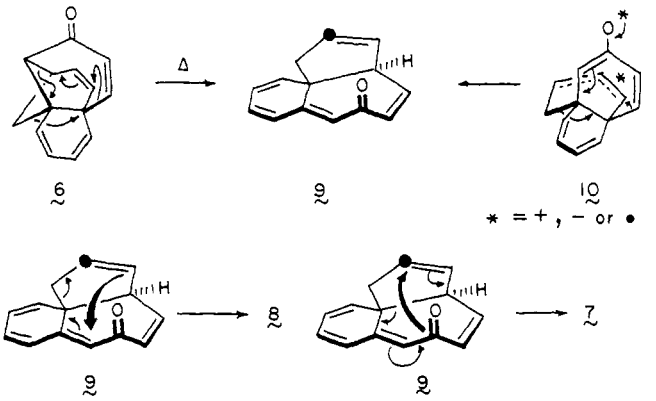
Scheme I



a thermodynamically driven propensity for aromatization of the cyclohexadiene ring was anticipated (note that two C–C bonds must be cleaved to achieve this result), covalent incorporation of the carbonyl group with loss of the stability normally associated with a C–O double bond was not. With reference to Scheme II, this unusual behavior may be interpreted most cogently in terms of pentaenone **9**. Although **6** may be economically isomerized to **9** by three simple antiperiplanar carbon shifts as illustrated, the process need not be concerted since stepwise alternatives, e.g., via intermediate **10**, appear readily accessible. Dreiding models of **9** make clear two relevant facts: (a) strikingly, the carbonyl oxygen is positioned at a distance only 3.3 Å away from the dotted olefinic carbon atom in a geometric relationship particularly conductive to $p\pi$–$p\pi$ overlap; (b) aromatization can be achieved by Cope rearrangement involving unsaturated centers initially 3.7 Å distant. While the latter process likely proceeds concertedly according to the dictates of orbital symmetry (six-electron sigmatropy),[7] the requisite reorganization of eight electrons to arrive at **7** (Scheme II) is not comparably favored. Nevertheless, the dominant formation of **7** (also with concurrent aromatization)

(7) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie, Academic Press: Weinheim/Bergstr., New York, 1970.

Scheme II



belies the preferred operation of this hypothetical pathway. For the present, the proximity and relative orientation of the carbonyl group in **9** is deemed responsible for this phenomenon. On this basis, it would be of considerable interest to examine the behavior of other sterically congested molecules structurally tailored for multichannel reactivity.

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Supplementary Material Available: Data collection and processing parameters, atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles in **7** (4 pages). Ordering information is given on any current masthead page.

Anthracycline Synthesis with Fischer Carbene Complexes[1]

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The clinical effectiveness of the anthracycline antitumor agents daunomycin (**5a**) and adriamycin (**5b**) has led to a substantial number of reports on the total synthesis of their corresponding aglycones, **6a** and **6b**.[2,3] The 11-deoxy analogues of **6a** and **6b** (R_4 = H) are of current interest due to improved therapeutic indices, and there have very recently been several reports on their total syntheses,[2,3b,4,5] We have envisioned an approach to an-

(1) This work was presented at the 186th National Meeting of the American Chemical Society, Washington, D.C., Aug 28-Sept 2, 1983.

(2) For comprehensive reviews see: "Anthracycline Antibiotics"; El Khadem, H. S., Ed.; Academic Press: New York, 1982. Arcamone, F. *Med. Chem. (Academic)* **1981**, *17*. Kametani, T.; Fukumoto, K. *Med. Res. Rev.* **1981**, *1*, 23–72.

(3) For more recent synthetic approaches, see: (a) Tamariz, J.; Schwager, L.; Stibbard, J. H. A.; Vogel, P. *Tetrahedron Lett.* **1983**, 1497. (b) Rao, A. V. R.; Reddy, K. B.; Mehendale, A. R. *J. Chem. Soc., Chem. Commun.* **1983**, 564. (c) Broadhurst, M. J.; Hassal, C. H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2227. (d) Kimball, S. D.; Kim, K. S.; Mohanty, D. K.; Vanotti, E.; Johnson, F. *Tetrahedron Lett.* **1982**, 3871. (e) Swenton, J. S.; Anderson, D. K.; Jackson, D. K.; Narasimhan, L. *J. Org. Chem.* **1981**, *46*, 4825. (f) Hauser, F. M.; Prasanna, S. *J. Am. Chem. Soc.* **1981**, *103*, 6378. (g) Dolson, M. G.; Chenard, B. L.; Swenton, J. S. *Ibid.* **1981**, *103*, 5263.

(4) (a) Hauser, F. M.; Prasanna, S.; Combs, D. W. *J. Org. Chem.* **1983**, *48*, 1328. (b) Rao, A. V. R.; Mehendale, A. R.; Reddy, K. B. *Tetrahedron Lett.* **1982**, 2415. (c) Rao, A. V. R.; Deshpande, V. H.; Reddy, N. L. *Ibid.* **1982**, 775. (d) Jung, M. E.; Node, M.; Pfluger, R. W.; Lyster, M. A.; Lowe, J. A., III *J. Org. Chem.* **1982**, *47*, 1150. (e) Gesson, J. P.; Mondon, M. *J. Chem. Chem. Commun.* **1982**, 421. (f) Alexander, J.; Flynn, D. L.; Mitscher, L. A.; Veysoglu, T. *Tetrahedron Lett.* **1981**, 3711. (g) Kimball, S. D.; Walt, P. R.; Johnson, F. *J. Am. Chem. Soc.* **1981**, *103*, 1561. (h) Yadau, J.; Corey, P.; Hsu, C. T.; Perlman, K.; Sih, C. *J. Tetrahedron Lett.* **1981**, 811.

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