Table I. Calculated Transition-State Ionization Potentials for $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$

orbital	calculated IP, eV	assignment	exptl[a]
$11b_1$	5.58	U 5f	6.64 (x)
$9b_2$	6.30	U-CH_3	7.26 (a)
$13a_1$	6.50		
$10b_1$	7.08	U-C_5H_5 (π_2)	7.74
$8b_2$	7.22		8.16
$6a_2$	7.25		8.45 (b,c)
$12a_1$	7.30		
$9b_1$	10.24	C_5H_5 (π_1)	10.64 (d)

[a] Experimental values in eV for $(\eta^5\text{-}C_5Me_5)_2U(CH_3)_2$ from ref 7. The band labels from that reference are given in parentheses.

Table II. Calculated Transition-State Ionization Potentials for $(\eta^5\text{-}C_5H_5)_2UCl_2$

orbital	calculated IP, eV	assignment	exptl[a]
$11b_1$	6.38	U 5f	6.85 (x)
$9b_2$	7.25	U-C_5H_5 (π_2)	7.47 (a)
$13a_1$	7.40		7.88 (a')
$10b_1$	7.49		
$6a_2$	7.62		
$8b_2$	9.71	Cl lone pair	10.10 (b)
$5a_2$	9.92		10.65 (c)
$9b_1$	9.94		
$12a_1$	10.14		
$11a_1$	10.24	U-Cl	10.90 (c')
$7b_2$	10.42		

[a] Experimental values in eV for $(\eta^5\text{-}C_5Me_5)_2UCl_2$ from ref 7. The band labels from that reference are given in parentheses.

energies than do the U–Cl bonds. There is no evidence that Cl^- acts as a π-donor to U in $(\eta^5\text{-}C_5H_5)_2UCl_2$.

The highest lying two electrons of each complex occupy orbitals that are essentially pure U 5f atomic orbitals. In order to simplify the calculations and to test the efficacy of the Xα-SW method applied to f orbital systems, we have required both of these electrons to occupy the same orbital, i.e., we have treated the complexes as closed-shell molecules. Even with this restriction the seven 5f orbitals are clustered quite closely together, and it is apparent that the molecule will prefer an open-shell, high-spin configuration for these last two electrons. This is consistent with the observed paramagnetism of the complexes.[14] As a further test, we have performed an Xα-SW calculation on the isostructural d^2 system $(\eta^5\text{-}C_5H_5)_2MoCl_2$, which is diamagnetic.[15] In this case, there is a healthy 2.2-eV gap between the HOMO and the LUMO, consistent with the preferred singlet spin properties of the Mo complex. Thus, the Xα-SW method correctly predicts the magnitude of both f and d orbital splitting in these bent metallocene molecules.

Ionization potentials for $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)_2UCl_2$ have been calculated using Slater's transition-state formalism.[16] The calculated ionization potentials are compared to the experimental values obtained by Fragala, Marks, et al.,[7] in Tables I and II. Even without the explicit inclusion of spin-orbit effects, the results are very satisfying. As is typical for Xα-SW calculations, the calculated ionization potentials are uniformly too low. The splittings between the various IP's are in excellent accord with the experimental ones, however, indicative that the RXα method properly estimates the extent of U–ligand interaction. The assignments presented here are in concurrence with those derived from the analysis of the relative He(I) and He(II) photoionization intensities with the exception of the band at 10.0–10.7 eV in the spectrum of $(\eta^5\text{-}C_5Me_5)_2U(CH_3)_2$. This was proposed to be one of the ionizations due to the U–CH_3 bonds.[7] We find only a small splitting (~0.20 eV) between the two U–CH_3 ionizations and prefer that the band at 10.0–10.7 eV be assigned to ionizations from the totally symmetric π orbital of the $\eta^5\text{-}C_5Me_5$ rings.

Acknowledgment. We are grateful to Professors T. J. Marks and V. W. Day for results prior to publication. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. $(\eta^5\text{-}C_5H_5)_2U(CH_3)_2$, 87136-09-2; $(\eta^5\text{-}C_5H_5)_2UCl_2$, 11077-15-9; $(\eta^5\text{-}C_5Me_5)_2U(CH_3)_2$, 67605-92-9; $(\eta^5\text{-}C_5Me_5)_2U(Cl_2)$, 67506-89-2; $(\eta^5\text{-}C_5H_5)_2MoCl_2$, 12184-22-4.

---

[14] Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.

[15] Cooper, R. L.; Green, M. L. H. *J. Chem. Soc. A* **1967**, 1155.

[16] Slater, J. C. "Quantum Theory of Molecules and Solids. The Self-Consistent Field for Molecules and Solids"; McGraw-Hill: New York, 1974; Vol. 4.

Tricarbon Monoxide

Ronald D. Brown,* Frank W. Eastwood, Patricia S. Elmes, and Peter D. Godfrey

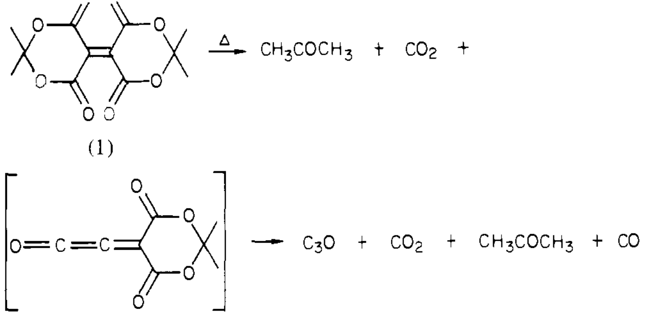
Monash University
Clayton, Victoria, Australia 3168

Received July 11, 1983

We wish to report the generation and identification of the gas-phase species C_3O. In 1971[1] DeKoch and Weltner reported the appearance of an IR absorption at 2241 cm^{-1} by reaction of C atoms with CO in an Ar matrix, attributing this band to C_3O. No further evidence in support of this assignment appears to have been forthcoming. Berke and Härter[2] described a chromium carbonyl complex containing C_3O as a ligand but did not observe C_3O as a separate species.

We set out to generate C_3O directly by an application of the pyrolytic decomposition pathway for Meldrum's acid and its derivatives[3] that has previously been exploited to generate and spectroscopically characterize propadienone, C_3H_2O.[4] Compound **1** was prepared[5] and pyrolyzed in a quartz tube of 20-mm i.d. × 400-mm length attached to a quadrupole mass spectrometer and microwave spectrometer cell.

As expected, at 500 °C **1** decomposed to yield acetone, CO_2, and some CO (detected in the QMS). At temperatures of 600 °C and higher a peak at m/z 52 appeared. At this temperature the mass spectrum showed some increase in peaks due to acetone, CO_2, and CO.



In the microwave spectrometer all of the stronger lines of acetone were observed under these conditions. In addition some weak lines, which increased in intensity as the pyrolysis tem-

---

[1] DeKock, R. L.; Weltner, W. *J. Am. Chem. Soc.* **1971**, *93*, 7106-7107.

[2] Berke, H.; Härter, P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 225-226.

[3] Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J. *Aust. J. Chem.* **1974**, *27*, 2373-2384.

[4] Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L. *J. Am. Chem. Soc.* **1976**, *98*, 7421-7422; *Aust. J. Chem.* **1977**, *30*, 179-193. Blackman, G. L.; Brown, R. D.; Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L. *J. Mol. Spectrosc.* **1977**, *68*, 488-491. Brown, R. D.; Godfrey, P. D.; Champion, R.; McNaughton, D. *J. Am. Chem. Soc.* **1981**, *103*, 5711-5715; **1982**, *104*, 6167. Brown, R. D. *J. Mol. Struct.* **1983**, *97*, 293-302.

[5] Snyder, H. R.; Kruse, C. W. *J. Am. Chem. Soc.* **1958**, *80*, 1942-1944.

0002-7863/83/1505-6496$01.50/0

Table I. Microwave Transition Frequencies of C_3O^a

transition	frequency/MHz^b
$1 \leftarrow 0$	9621.762
$2 \leftarrow 1$	19243.531
$3 \leftarrow 2$	28865.227
$4 \leftarrow 3$	38486.862
$5 \leftarrow 4$	48108.504
$6 \leftarrow 5$	57729.962

^{a} $B_0 = 4810.885$ (33); $D_J = 0.000740$ (65) MHz. ^{b} Estimated uncertainties in measured frequencies are 20 kHz.

perature was increased to 1000 °C, were observed at frequencies very close (1 part in 600) to those predicted for C_3O by ab initio molecular orbital calculations (full geometry optimization by GAUSSIAN 80 SCFMO calculations at the MP3/6-31G* level).[6] Our observed frequencies and J assignments, together with least-squares-fitted rotational and centrifugal distortion constants consistent with a linear molecule, are given in Table I. The observed Stark splitting patterns support these assignments. From the Stark effect we were able to determine the dipole moment of the species to be 2.391 (5) D.

The present observations are fully consistent with the presence of a gas-phase molecule of formula C_3O and electronic structure well represented by the classical resonance form $^-C{\equiv}C{-}C{\equiv}O^+$. We have not been able to account for the microwave spectral observations in any alternative way, and the spectrum, together with the observation of a m/z peak 52 in the mass spectrum, seems conclusive. Rough lifetime measurements in the microwave waveguide cell indicate a lifetime of less than 1 s at about 1 Pa total pressure.

We are currently investigating isotopic species and other properties of C_3O.[7]

---

(6) Brown, R. D.; Rice, E., submitted for publication.

(7) Robert Champion assisted with some preliminary experiments. We are grateful to Dr. Roger F. C. Brown for helpful discussions about preparative aspects of this project. The work was supported by a grant from the Australian Research Grants Scheme.

Reaction of Bicyclic Endoperoxides with Carbonyl Compounds. A New Approach to 1,2,4-Trioxanes

Charles W. Jefford,* Danielle Jaggi, John Boukouvalas, and Shigeo Kohmoto

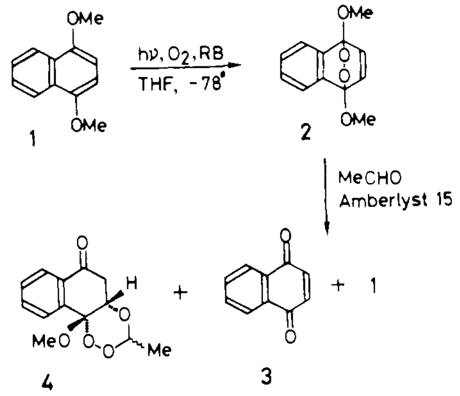
Department of Organic Chemistry, University of Geneva
1211 Geneva 4, Switzerland

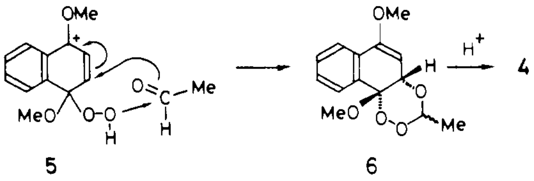
Received April 5, 1983

Bicyclic 1,4-endoperoxides are easily accessible by several reactions, of which the [4 + 2] addition of singlet oxygen to a cyclic 1,3-diene is typical.[1] Their preparation, originating with the pioneering work of Dufraisse,[2] and properties have been studied for some 57 years. However, it appears that the chemistry of 1,4-endoperoxides has been confined to their reduction,[3] cleavage,[4] fragmentation,[4] and rearrangement.[5] Interesting though these processes[6] may be, few, if any, reactions with organic molecules have been recorded.

We now wish to report a new reaction of bicyclic 1,4-endoperoxides that has potential for the synthesis of a variety of 1,2,4-trioxanes. We have chosen three readily available endoperoxides to demonstrate the power of the method.

The first example is the peroxide **2** obtained by the rose bengal sensitized photooxygenation of 1,4-dimethoxynaphthalene (**1**) in THF at −78 °C.[7] To the resulting solution of **2** an excess of acetaldehyde together with amberlyst-15 resin as catalyst was added. After the mixture was stirred at −78 °C overnight, workup afforded three products. The first two **1** (24%) and **3** (37%) are a consequence of the inherent thermal and chemical instability of the peroxide **2**.[8] However, the third product **4** is the cis-fused 1,2,4-trioxane (13%) consisting of a pair of epimers. What has happened, we believe, is that protonation of **2** has generated the hydroperoxide **5** as the crucial first step. Normally, its hydrolysis is easy, giving 1,4-naphthoquinone (**3**). However, **5** has the chance to nucleophilically attack the acetaldehyde molecule, which in turn cyclizes to the 1,2,4-trioxane ring, which is cis-fused for reasons of geometry control. The resulting product **6** is hydrolyzed in situ to **4**, which consists of a pair of epimers.[9]





---

(1) Gollnick, K.; Schenck, G. O. In "1,4-Cycloadditions"; Hamer, J., Ed.; "Oxygen as Dienophile"; Academic Press: New York, 1967; Chapter 10, pp 255–344. Denny, R. W.; Nickon, A. *Org. React.* (*N.Y.*) **1973**, *20*, 133–336. Saito, I.; Matsuura, T. In "Singlet Oxygen"; Wasserman, H. H.; Murray, R. W., Eds.; "The Oxidation of Electron-Rich Aromatic Compounds"; Academic Press: New York, 1979, Chapter 10, pp 511–574.

(2) Moureu, C.; Dufraisse, C.; Dean, P. M. *C. R. Séances Acad. Sci.* **1926**, *182*, 1440, 1584.

(3) Adam, W.; Klug, G. *Tetrahedron Lett.* **1982**, *23*, 3155. Klärner, F.-G.; Schmidt, E. K. G.; Rahman, M. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 138. Baeckström, P.; Okecha, S.; de Silva, N.; Wijekoon, D.; Norin, T. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 31. Adam, W.; Rodriguez, A. *Tetrahedron Lett.* **1981**, *22*, 3509. Adam, W.; Cueto, O.; De Lucchi, O.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *J. Am. Chem. Soc.* **1981**, *103*, 5822.

(4) Graziano, M. L.; Iesce, M. R.; Carli, B.; Scarpati, R. *Synthesis* **1983**, 125. Sakuragi, H.; Furusawa, G.; Ueno, K.; Tokumaru, K. *Chem. Lett.* **1982**, 1213. Rigaudy, J.; Scribe, P.; Brelière, C. *Tetrahedron* **1981**, *37*, 2585.

(5) Feringa, B. L.; Butselaar, R. J. *Tetrahedron Lett.* **1983**, *24*, 1193. Balci, M.; Sütbeyaz, Y. *Ibid.* **1983**, *24*, 311. Graziano, M. L.; Iesce, M. R.; Carli, B.; Scarpati, R. *Synthesis* **1982**, 736. Castedo, L.; Estêvez, R. J.; Saa, J. M.; Suau, R. *J. Heterocycl. Chem.* **1982**, *19*, 1469. Feringa, B. L.; Butselaar, R. J. *Tetrahedron Lett.* **1982**, *23*, 1941. Knoechel, T.; Pickl, W.; Daub, *J. Chem. Soc., Chem. Commun.* **1982**, 337. Kumagai, T.; Tokida, A.; Kidoura, K.; Seshimoto, O.; Mukai, T. *Tetrahedron Lett.* **1982**, *23*, 873. Saito, I.; Nagata, R.; Kotsuki, H.; Matsuura, T. *Ibid.* **1982**, *23*, 1717. Rang, H.-S.; Foote, C. S. *Ibid.* **1982**, *23*, 2551. Zagorski, M. G.; Salomon, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 3498. Murai, A.; Ono, M.; Abiko, A.; Masamune, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1195. Beauhaire, J.; Fourrey, J.-L. *J. Chem. Soc., Perkin Trans. 1* **1982**, 861. Hagenbuch, J.-P.; Birbaum, J.-L.; Métral, J.-L.; Vogel, P. *Helv. Chim. Acta* **1982**, *65*, 887. Matsumoto, M.; Kuroda, K.; Suzuki, Y. *Tetrahedron Lett.* **1981**, *22*, 3253. Suzuki, M.; Oda, Y.; Noyori, R. *Ibid.* **1981**, *22*, 4413. For an account of the rearrangement of 1,4-endoperoxides to 1,2-dioxetanes and epoxides, see: Schaap, A. P.; Zaklika, K. A. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Chapter 7, pp 243–286. Saito, I.; Matsuura, T. In "Singlet Oxygen"; H. H., Wassermann, R. W., Murray, Eds.; Academic Press: New York, 1979; Chapter 10 pp 511–574.

(6) Balci, M. *Chem. Rev.* **1981**, *81*, 91.

(7) Rigaudy, J.; Deletang, C.; Basselier, J.-J. *C. R. Seances Acad. Sci., Ser. C* **1969**, *C268*, 344.

(8) Peroxide **2** readily undergoes retro Diels–Alder reaction to give **1**. Moreover, **2** is also prone to acid hydrolysis to the quinone **3** (cf.: Rigaudy, J.; Sparfeld, D. *Bull. Soc. Chim. Fr.* **1972**, 3441–3446).

0002-7863/83/1505-6497$01.50/0