

cyclopropyltrioxorhenium yields a catalyst with H₂O₂ that is stable at elevated temperatures and even more active in epoxidation than the MTO derivative 2.

Experimental Procedure

2: MTO (1.00 g, 4 mmol) was dissolved in distilled water (20 mL) at 25 °C. The solution was cooled to 0 °C, and perhydrol p.A. (5 mL of 30% H₂O₂) was added dropwise. After 10 min the yellow-orange solution was extracted with diethyl ether (50 mL). The ether extract was washed with water (3 × 20 mL) and dried twice with Na₂SO₄, and finally over 4 Å molecular sieves. (These operations should be performed as rapidly as possible to avoid decomposition.) The organic phase was quickly evaporated to dryness at 0 °C under high vacuum. The yellow residue was washed with *n*-pentane at 0 °C and finally dissolved in dichloromethane (if necessary with addition of a little diethyl ether). Analytically pure product was obtained on crystallization at -30 °C. Yield 960 mg (80%). Single crystals of **3** were obtained after addition of a small amount of diglyme to solutions of **2** in a mixture of diethyl ether and *n*-pentane (1:25) and slow cooling to -30 °C in screw-top vials that were not tightly closed.

Received: March 8, 1993 [Z 5908 IE]
German version: *Angew. Chem.* **1993**, *105*, 1209

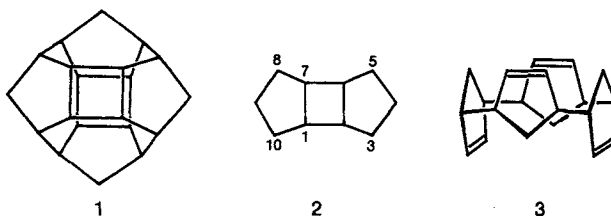
- [1] Surveys: a) R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, **1981**; b) *Organic Syntheses by Oxidation with Metal Compounds* (Eds.: W. J. Mijs, C. R. H. I. de Jonge), Plenum, New York, **1986**; c) R. A. Sheldon in *Aspects of Homogeneous Catalysis, Vol. 4*, (Ed.: R. Ugo), Reidel, Dordrecht, **1981**, p. 3 ff.; d) H. A. Jørgensen, *Chem. Rev.* **1989**, *89*, 431–458.
- [2] a) W. A. Herrmann, R. W. Fischer, D. W. Marz, *Angew. Chem.* **1991**, *103*, 1706–1709; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1638–1641; b) W. A. Herrmann, D. W. Marz, W. Wagner, J. Kuchler, G. Weichselbaumer, R. W. Fischer (Hoechst AG), DE-B 3.902.357, **1989/1990**; c) R. W. Fischer, *GIT Fachz. Lab.* **1992**, *10*, 997–1002; d) W. A. Herrmann, R. W. Fischer, M. U. Rauch, W. Scherer, *J. Mol. Catal.* **1993**, in press.
- [3] **2:** Yellow, hygroscopic crystals; m.p. 55 °C, decomp. 65 °C. IR (CH₂Cl₂ or Nujol(*), {[CH₃ReO(O₂)₂ · D₂O], ca. 90%}: $\tilde{\nu}(\text{ReO})[\text{cm}^{-1}] = 1020$ (vs) [2 × 1020 (vw)]; $\tilde{\nu}(\text{Re-O}_2)^* = 330$ {328} (w); $\delta(\text{Re-OH}) = 1121$ {800} (w); $\tilde{\nu}(\text{O}_2) = 877$; $\tilde{\nu}(\text{Re-CH}_3) = 571$ {572} (s); CH₃ rocking mode: 814 (w); $\tilde{\nu}(\text{H}_2\text{O}) = 3616, 3536$ {2634} (vs); $\delta(\text{H}_2\text{O}) = 1599$ {1180} (s); $\delta(\text{HDO}) = 1430$ (w); $\delta(\text{H}_3\text{O}^+) = 1752$ {1282} (w); $\nu_{\text{asym}}(\text{CH}_3) = 3058$ {3055} (s); $\nu_{\text{sym}}(\text{CH}_3) = 2968$ {2987} (s); $\delta_{\text{asym}}(\text{CH}_3) = 1399$ {1403} (m); $\delta_{\text{sym}}(\text{CH}_3) = 1213$ {1217}. ¹H NMR (400 MHz, D₂O, 20 °C, {[D₈]THF, -20 °C}): $\delta = 2.6$ (CH₃, s) {2.71 (CH₃, s), 9.4 (H₂O-coord., br)}; ¹³C{¹H} NMR (100.5 MHz, D₂O, 20 °C): $\delta = 31$. ¹³C NMR (100.5 MHz, [D₈]THF, -10 °C): $\delta = 30.53$ (q, ²J(¹³C, ¹H) = 135 Hz); ¹⁷O NMR (54.21 MHz, -20 °C, Et₂O): $\delta = 762$ (ReO), 422 and 363 (η^2 -O₂, signal width 1250 Hz), -26 (H₂O). UV/VIS (Et₂O, 20 °C): $\lambda_{\text{max}} = 364$ nm, $\epsilon = 700$ Lmol⁻¹cm⁻¹. MS (EI, 70 eV, ¹⁸⁷Re, correct isotope pattern): *m/z*: 282 [M - H₂O], 250 [CH₃ReO₃], 220 [HReO₂, M - H₂O - H₂CO, base peak]; (CI, isobutane, ¹⁸⁷Re, correct isotope pattern): *m/z*: 299 [M + 1 - H₂], 281 [M + 1 - H₂ - H₂O, base peak]. Correct elemental analysis (C,H,O,Re).
- [4] A little decomposition occurs during the NMR experiment.
- [5] Yellow-orange, slightly hygroscopic crystals. M.p. 40 °C. ¹H NMR (400 MHz, [D₈]THF, 20 °C): $\delta = 2.66$ (Re-CH₃, s, 3H), 3.27 (CH₃, s, 6H), 3.43 (CH₂, t, 4H), 3.52 (CH₂, t, 4H), 3.39 (H₂O/CH₃OH; from decomposition, br). MS (EI, 70 eV, ¹⁸⁷Re, correct isotope pattern): *m/z*: 266 [CH₃Re(O₂)₂], 250 [CH₃ReO₃], 89 [C₄H₉O₂], 59 [C₃H₇O, base peak], *M*⁺ not observed. Correct elemental analysis (C,H,O,Re).
- [6] **3:** C₂₀H₂₄O₂Re; *a* = 1246.4(2), *b* = 1496.4(3), *c* = 714.9(1) pm, *V* = 1333 × 10⁶ pm³, measurement at -80 °C, $\rho_{\text{calc}} = 2.16$ gcm⁻³, $\mu = 92.7$ cm⁻¹, *Z* = 4, orthorhombic, *Pnma* (no. 62), Enraf-Nonius CAD4, $\lambda = 71.07$ pm (MoK α , graphite monochromator), ω scan; of 3002 measured reflections (+ *h*, + *k*, ± *l*), 1211 were independent, and 1104 with *I* > 3 σ (*I*) were used for the refinement; structure solution with Patterson methods and difference Fourier syntheses, empirical absorption correction on the basis of psi scan data, transmission coefficients 0.608–0.999, 125 refined parameters, all H atoms found and refined freely with isotropic auslenkung parameters. $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.019$, $R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2 = 0.021$, residual electron density +1.75, -0.99 $\Delta e_s/\text{\AA}^3$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-57189, the names of the authors, and the journal citation.
- [7] W. A. Herrmann, W. R. Thiel, J. G. Kuchler, J. Behm, E. Herdtweck, *Chem. Ber.* **1990**, *123*, 1963–1970.
- [8] a) P. Legzdins, E. C. Phillips, S. J. Rettig, L. Sánchez, J. Trotter, V. C. Yee, *Organometallics* **1988**, *7*, 1877–1878. b) H. Mimoun in *The Chemistry of Functional Groups, Peroxides* (Ed.: S. Patai), Wiley, New York, **1983**, Chap. 15; c) M. J. Nolte, E. Singleton, M. Laing, *J. Am. Chem. Soc.* **1975**,

- 97, 6396–6400, and references therein; d) G. Henrici-Olivé, S. Olivé, *Angew. Chem.* **1974**, *86*, 1–12; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 29–38.
- [9] W. A. Herrmann, C. C. Romão, R. W. Fischer, P. Kiprof, C. de Méric de Bellefon, *Angew. Chem.* **1991**, *103*, 183–185; *Angew. Chem. Int. Ed. Engl.* **1991**, *31*, 185–186.
- [10] W. A. Herrmann, P. Watzlowik, P. Kiprof, *Chem. Ber.* **1991**, *124*, 1101–1106.
- [11] *k*₁ was calculated on the basis of pseudo-first-order kinetics (olefin in excess) for the reaction **2** + olefin → **4** (*c*(olefin) = 2 × 10⁻¹ molL⁻¹, *c*(**2**) = 2 × 10⁻³ molL⁻¹); *k*₂ (*c*(**1**) = 1.1 × 10⁻³ molL⁻¹, *c*(H₂O₂) = 1 × 10⁻¹ molL⁻¹), and *k*₄ (*c*(**4**) = 1.6 × 10⁻³ molL⁻¹, *c*(H₂O₂) = 2.9 × 10⁻¹ molL⁻¹) were determined analogously. The reaction **2** → **4** (*k*₃) is first order. *E* = extinction; *S*_i = initial spectrum, *S*_f = final spectrum.
- [12] a) M. Postel, C. Brevard, H. Arzoumanian, J. G. Riess, *J. Am. Chem. Soc.* **1983**, *105*, 4922–4926; b) I. P. Gerathanassis, M. Momenteau, *ibid.* **1987**, *109*, 6944–6947; c) B. I. P. Gerathanassis, M. Momenteau, B. Loock, *ibid.* **1989**, *111*, 7006–7012; d) S. Berger, S. Braun, H.-O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen, Band 1* (Grundlagen, ¹⁷O-, ³³S- und ¹²⁹Xe NMR-Spektroskopie), Thieme, Stuttgart, **1992**, p. 107 ff., and references therein.

Golcondane: A Novel, Caged, Nonacyclic C₂₀H₂₄-Hydrocarbon of D_{2d} Symmetry**

By Goverdhan Mehta* and S. Hari Krishna Reddy

The conception and creation of space-enclosing polycyclic hydrocarbons (polyhedranes) of novel shape and symmetry is an area of contemporary interest that elegantly blends aesthetics with synthetic challenge.^[1] In recent years, the assembly of C₂₀-polyhedranes in particular received a great deal of attention from organic chemists and culminated in many notable achievements. These include the syntheses of C₂₀H₂₀-dodecahedrane by Paquette et al.^[2a] and Prinzbach et al.,^[2b] C₂₀H₂₀-pagodane by Prinzbach et al.,^[2c] and C₂₀H₂₄-propella[3₄]prismane by Gleiter et al.^[2d] to mention a few.



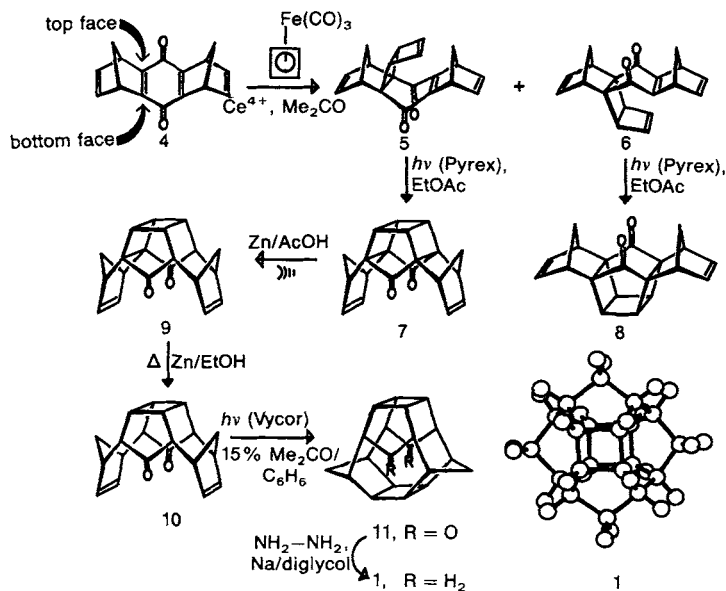
Through this communication, we add a new member to this esoteric C₂₀-family and describe a short synthesis of a nonacyclic C₂₀H₂₄-hydrocarbon **1** ("golcondane")^[3] of D_{2d} symmetry. Interestingly, the polycyclic ring system of **1** could be regarded either as a dimer of *cis,syn,cis*-tricyclo-[5.3.0.0^{2,6}]decane (**2**) with an orthogonal union of the two units through C₃, C₅, C₈, and C₁₀ or as a subsequent product of a head-to-tail, cyclic 1,4 tetramer of 1,3-cyclopent-

[*] Prof. G. Mehta, S. H. K. Reddy
School of Chemistry, University of Hyderabad
Hyderabad 500134 (India)
Telefax: Int. code + (842)253145
and
Jawaharlal Nehru Center for Advanced Scientific Research
Indian Institute of Science Campus
Bangalore 560012 (India)

[**] We thank the Indian National Science Academy (award of Ramanujan Research Professorship to GM) and the Council for Scientific and Industrial Research (CSIR; award of a Research Fellowship to SHKR). We thank Dr. D. S. K. Reddy and Dr. M. S. Reddy for their interest.

tadiene (3), in which the diametrically opposite pairs of double bonds have undergone [2 + 2] ring closure.

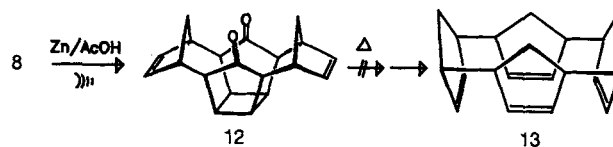
Reaction between *syn*-bisorborneno-1,4-benzoquinone (4)^[4] and cyclobutadiene (liberated from its iron tricarbonyl complex with ceric ammonium nitrate) furnished two [4 + 2] *endo* adducts 5^[5, 6] and 6^[5, 6] in a 55:45 ratio and 70% yield. On irradiation with a Hanovia 450 W Hg lamp through a pyrex filter, 5 and 6 underwent smooth intramolecular [$\pi_s^2 + \pi_s^2$] ring closure to give nonacyclic, annulated bishomocubane diones 7^[5] and 8^[5] (61%) and 35%, respectively. The bishomocubane moiety in 7 was opened through the reductive scission of cyclobutyl bonds conjugating the 1,4-dicarbonyl functionality.^[8] Thus, reaction of 7 with Zn in acetic acid under ultrasonication furnished 9^[5] and 10^[5] (16:1, 85%). The octacyclic dione 9 in which one bond has been cleaved could be transformed to heptacycle 10^[5] on further exposure to Zn in ethanol in 30–40% yield. Alterna-



Scheme 1.

tively, 10 could be accessed directly from 7 in a single-pot reaction with Zn in ethanol, albeit in somewhat lower yield (about 25%). The reductive opening of the cage in 7 rendered the two double bonds proximal, and irradiation of 10 from a 450 W Hanovia lamp led to the desired intramolecular [2 + 2] cycloaddition, and the nonacyclic dione 11^[5] was readily realized. Its structure was secured through X-ray crystal structure determination.^[9] Deoxygenation of 11 presented considerable difficulties, but eventually a modified Wolff–Kishner reduction could be carried out to furnish the C₂₀H₂₄-hydrocarbon, golcondane (1, 10–20%),^[5] which as expected exhibited a 3-line ¹³C NMR spectrum ($\delta = 45.63, 41.04, 39.21$), while 11 showed a 6-line ¹³C NMR spectrum. The energy-minimized structure of 1 determined with MMX force-field calculations (Scheme 1, strain energy = 132.4 kcal mol⁻¹, $\Delta H_f^\circ = 74.9$ kcal mol⁻¹) exhibited structural parameters closely resembling those for its precursor dione 11 obtained by X-ray studies.

The nonacyclic, annulated bishomocubanedione 8 on zinc/acetic acid reduction also furnished the corresponding heptacyclic dione 12 (50%) through reductive scission of two C–C bonds. Several attempts at thermal [2 + 2] cycloreversion in 12 to furnish the novel head-to-head 1,4-cyclic tetramer 13 of 1,3-cyclopentadiene have not borne fruit so far



Scheme 2.

(Scheme 2). Nonetheless, 10 and 12 are potential precursors for 3 and 13, respectively, besides many other novel polycycles. These possibilities are currently being explored.

Received: January 26, 1993 [Z 5830 IE]
German version: *Angew. Chem.* 1993, 105, 1230

- [1] a) *Cage Hydrocarbons* (Ed.: G. Olah), Wiley, New York, 1990; b) *Carbocyclic Cage Compounds. Chemistry and Applications* (Eds.: E. Osawa, O. Yonemitsu), VCH Publishers, New York, 1992; c) N. Anand, T. S. Bindra, S. Ranganathan, *Art in Organic Synthesis*, 2nd ed., Wiley, New York, 1988.
- [2] a) Review: L. A. Paquette, *Chem. Rev.* 1989, 89, 1051; b) review: W. D. Fessner, H. Prinzbach in *Organic Synthesis, Modern Trends* (Ed.: O. Chizov), Blackwell, Oxford, 1987, p. 23; c) W. D. Fessner, G. Sedelmeier, P. R. Spurr, G. Rihs, H. Prinzbach, *J. Am. Chem. Soc.* 1987, 109, 4626; d) R. Gleiter, M. Karcher, *Angew. Chem.* 1988, 100, 851; *Angew. Chem. Int. Ed. Engl.* 1988, 27, 840.
- [3] In honor of the 400th anniversary of the founding of the city of Hyderabad, in Southern India, we have named 1 as golcondane, derived from Golconda, the old name of Hyderabad; see the *New Oxford Encyclopedic Dictionary*, Bay Books, Oxford University Press, Oxford, 1983, p. 720. IUPAC nomenclature for 1: Nonacyclo[10.7.1.0^{2,6}.0^{4,17}.0^{5,8}.0^{7,11}.0^{9,15}.0^{13,19}.0^{14,18}]icosane.
- [4] a) G. Mehta, S. Padma, S. R. Karra, K. R. Gopidas, D. R. Cyr, P. K. Das, M. V. George, *J. Org. Chem.* 1989, 54, 1342; b) G. Mehta, S. H. K. Reddy, *Tetrahedron Lett.* 1991, 32, 4989.
- [5] All new compounds were characterized on the basis of ¹H and ¹³C NMR spectra and analytical data (MS and/or elemental analysis). ¹³C NMR data in CDCl₃ for some key compounds: 1: ¹³C NMR (50 MHz): $\delta = 45.63, 41.04, 39.21$; 5: ¹³C NMR (25.0 MHz): $\delta = 197.71, 170.60, 142.83, 140.18, 136.95, 73.88, 62.76, 49.29, 49.00, 48.47, 42.41$; 6: ¹³C NMR (25.0 MHz): $\delta = 197.66, 171.00, 143.18, 138.06, 136.24, 72.65, 62.41, 50.59, 49.82, 48.65, 48.29$; 7: ¹³C NMR (25.0 MHz): $\delta = 213.07, 134.95, 65.71, 45.06, 43.53, 38.35$; 8: ¹³C NMR (25 MHz): $\delta = 214.60, 136.58, 66.88, 49.82, 41.76, 37.41$; 10: ¹³C NMR (25.0 MHz): $\delta = 222.95, 134.41, 58.06, 41.88, 41.76, 35.17$; 11: ¹³C NMR (25.0 MHz): $\delta = 219.48, 54.06, 42.35, 41.94, 38.00, 36.41$.
- [6] The stereochemistry of 5 and 6 follows from the analyses of ¹H NMR data and chemical transformations. Further confirmation was obtained through the X-ray crystal structure determination of an interesting photoproduct derived from 5; see, G. Mehta, S. H. K. Reddy, V. Pattabhi, *J. Chem. Soc. Chem. Commun.* 1992, 991.
- [7] Besides 7, minor photoproduct(s) resulting from β cleavage were also encountered during the photoirradiation.
- [8] E. Wenkert, J. E. Yoder, *J. Org. Chem.* 1970, 35, 2986; G. Mehta, K. S. Rao, *ibid.* 1985, 50, 5537.
- [9] The X-ray crystal structure of 11 was kindly determined by Prof. V. Pattabhi, Department of Biophysics, Madras University, Madras, and will be published elsewhere.

Decamercuration of Ruthenocene**

By Charles H. Winter,* Young-Hee Han,
Robert L. Ostrander, and Arnold L. Rheingold

The mercuration of transition metal cyclopentadienyl complexes has been largely limited to ferrocene and its

[*] Prof. Dr. C. H. Winter, Y.-H. Han
Department of Chemistry, Wayne State University
Detroit, MI 48202 (USA)
Telefax: Int. + (313) 577-1377

Dr. R. L. Ostrander, Prof. Dr. A. L. Rheingold
Department of Chemistry, University of Delaware
Newark, DE 19716 (USA)

[**] This work was supported by the Air Force Office of Scientific Research (F49620-93-1-0072 to C.H.W.).