after centrifugation was lyophilized. The residue was redissolved in 150 mL of H_2O, saturated with NaCl, acidified to pH 2 with concentrated HCl, filtered, and extracted continuously with ether for 24 h. The extract was evaporated under reduced pressure to a viscous oil, 2.34 g, consisting mainly of **1a** (by NMR analysis). The crude product was methylated (CH_2N_2) and distilled in a Kugelröhr apparatus, bp 110 °C (0.2 mm). The product showed only traces of impurities by GC. A portion of the main product separated by preparative GC had NMR ($CDCl_3$) and mass spectra identical with the spectra of **methyl (±)-2,3-dihydroxy-3-methylbutyrate.**[5]

Synthesis of (*E*)-[4,4,4-$^2H_3$]-3-methylcrotonic Acid and Its Incubation wtih *Ps. putida*. Methyl tetrolate [bp 52–53 °C (22 mm)] was prepared by treatment of tetrolic acid with excess CH_2N_2/ether. The product (6.78 g, 0.069 mol) was converted to methyl (*E*)-[4,4,4-$^2H_3$]-3-methylcrotonate, **2c**, 7.0 g (0.060 mol), by treatment with $Li(CD_3)_2Cu$, following a procedure closely analogous to that described[4a,8] for the preparation of ethyl (*Z*)-[4,4,4-$^2H_3$]-3-methylcrotonate. The NMR spectrum of **2c** had δ ($CDCl_3$) 1.90 (trace, ca. 0.1 H), 2.15 (3 H, d, J = 1.5 Hz), 3.63 (3 H, s), 5.54 (1 H, q, J = 1.5 Hz).

The product (7.0 g) was saponified by treatment with 2 N NaOH (50 mL), stirring at 25 °C for 40 h. Upon acidification (HCl), the precipitate was filtered, washed with cold H_2O, and air-dried, giving **2b**: 4.48 g; NMR δ ($CDCl_3$) 1.90 (ca. 0.1 H, d, J = 1.5 Hz), 2.18 (ca. 2.8 H, d, J = 1.5 Hz), 5.69 (1 H, q, J = 1.5 Hz), 11.08 (1 H, br s, D_2O exchangeable). An additional 1.15 g of **2b** was obtained by ether extraction of the aqueous filtrate.

The product (1.0 g in 10 mL of H_2O, adjusted to pH 7.4 with KOH) was incubated as previously described by *Ps. putida* cells from two 100-mL cultures, and the crude product (400 mg) was isolated as before. After purification by Kugelröhr distillation of the methylated product, **1c** (295 mg) was obtained. After removal of trace impurities by preparative GC, the product had NMR ($CDCl_3$ + D_2O) δ 1.22 (ca. 3 H, s), 1.30 (ca. 0.1 H, s), 3.75 (3 H, s), 4.93 (1 H, s).

Registry No. 1a, 63903-90-2; **1b**, 75347-92-1; **1c**, 75365-50-3; **2a**, 541-47-9; **2b**, 75347-93-2; **2c**, 75347-94-3; isovaleric acid, 503-74-2; methyl tetrolate, 23326-27-4.

Communications

Oxygen Functionalization in Cyclooctatetraene via Singlet Oxygenation: Synthesis and Transformations of *anti*-7,8-Dioxatricyclo[4.2.2.0^{2,5}]deca-3,9-diene, the Endoperoxide of the Bicyclic Valence Tautomer of Cyclooctatetraene

Summary: The novel endoperoxide of the bicyclic valence tautomer of cyclooctatetraene is prepared, characterized, and transformed into a series of new and valuable synthetic intermediates derived from the bicyclo[4.2.0]octa-2,4,7-triene skeleton via base-catalyzed isomerization and MnO_2 oxidation, thermolysis and mCPBA oxidation, triphenylphosphine deoxygenation, and exhaustive diimide reduction.

Sir: The fact that cyclooctatetraene (**1**) is inert toward singlet oxygenation, either via photosensitized[1] or chemical[2] generation of singlet oxygen, obliges indirect strategies for the synthesis of the desirable endoperoxides **2** (Scheme I). In the case of the synthetically more challenging endoperoxide **2b**, derived from bicyclic valence tautomer **1b**, the indirect sequence **1a** → **3** → **4** → **2b** (Scheme I) has also failed[3] since so far it has not been possible to debrominate the known[4] endoperoxide **4** under sufficiently mild conditions at which the peroxide linkage is preserved. Presently we report the preparation of the endoperoxide **2b** via the sequence **1a** → **3** → **1b** → **2b** (Scheme I) and its chemical transformations into a number of useful difunctionalized oxygen derivatives of the bicyclo[4.2.0]-octa-2,4,7-triene skeleton.

Analogous to Vogel et al.,[5] the dibromide **3** was debrominated with *n*-BuLi in diethyl ether at −60 °C. The resulting solution of the sufficiently stable bicyclic valence tautomer **1b** was submitted to photosensitized oxygenation at −30 °C for 2 h with tetraphenylphorphyrin (TPP) as the sensitizer and a 150-W sodium lamp as a light source. The endoperoxide **2b** was obtained quantitatively (mp 75–76 °C, recrystallized from a CH_2Cl_2/*n*-C_6H_{14} mixture; 85% yield).[6,7]

The chemical transformations of the novel endoperoxide **2b** are summarized in (Scheme II). For example, via pathway **2b** → **5** the known dienedione **5** was prepared in an overall 85% yield (mp 50–51 °C, after silica gel chromatography; lit.[4] mp 51–52 °C); however, our sequence **1a** → **3** → **1b** → **2b** → **5** entails considerably less work.[8] On the other hand, when a benzene solution of **2b** is heated[3b] at 100 °C for 1 h, the new diepoxide **6** was obtained quantitatively[6,9] (mp 105–107 °C, recrystallized from a CH_2Cl_2/*n*-C_6H_{14} mixture; 85% yield). Treatment with *m*-chloroperbenzoic acid (mCPBA) in CH_2Cl_2 led to the intriguing trioxide **7** in 70% yield (mp 209–210 °C, recrystallized from a CH_2Cl_2/n-C_6H_{14} mixture),[6,10] representing the first of a total of six trioxide isomers of the bicyclo[4.2.0]octa-2,4,7-triene valence isomer of cyclooctatetraene.[3b] An X-ray analysis of **7** (Dr. K. Peters, Max-Planck-Institut für Festkörperforschung, Stuttgart, for the X-ray determination; complete details will be disclosed in a full paper on this subject) reveals that the epoxy oxygens on the cyclohexane ring are syn to one another, but anti with respect to the cyclobutane ring, and that the epoxy oxygen on the cyclobutane ring is syn with

(1) (a) Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1. (b) Matsuura, T.; Horinaka, A.; Nakashima, R. *Chem. Lett.* **1973**, 887.

(2) Adam, W.; Cueto, O.; De Lucchi, O.; K.-H. Hill, unpublished results. The reaction of cyclooctatetraene with chemical singlet oxygen sources such as 1,4-dimethoxy-9,10-diphenylanthracene 1,4-endoperoxide at elevated temperature (ca. 100–120 °C) were so far unsuccessful.

(3) (a) Adam, W.; Balci, M.; De Lucchi, O., unpublished results. (b) Adam, W.; Balci, M. *Tetrahedron* **1980**, *36*, 833. Cf. eq 19, p 839, and ref 36 therein.

(4) Oda, M.; Kayama, Y.; Kitahara, Y. *Tetrahedron Lett.* **1974**, 2019.

(5) Vogel, E.; Kiefer, H.; Roth, W. R. *Angew. Chem.* **1964**, *76*, 432; *Angew. Chem., Int. Ed. Engl.* **1964**, 3, 442.

(6) All new compounds exhibited satisfactory elemental composition by combustion analysis.

(7) For **2b**: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.20 (q, 2 H), 4.59 (q, 2 H), 5.91 (s, 2 H), 6.20 (dd, 2 H); IR (CCl_4) 3120, 3060, 2970, 1375, 1300, 950, 920 cm^{-1}.

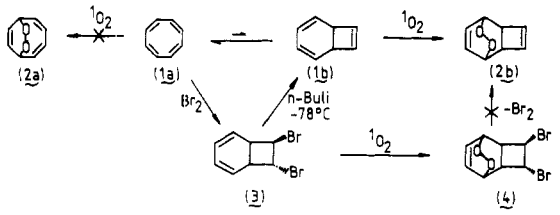
(8) Adam, W.; Balci, M.; Rivera, J. *Synthesis* **1979**, 807.

(9) For **6**: ^1H NMR ($CDCl_3$, Me_4Si) δ 3.10 (d, 2 H, J = 3 Hz), 3.30 (s, 2 H), 3.45 (d, 2 H, J = 3 Hz), 6.20 (s, 2 H); IR (KBr) 3130, 3000, 2915, 1580, 1420, 1060, 950, 860 cm^{-1}.

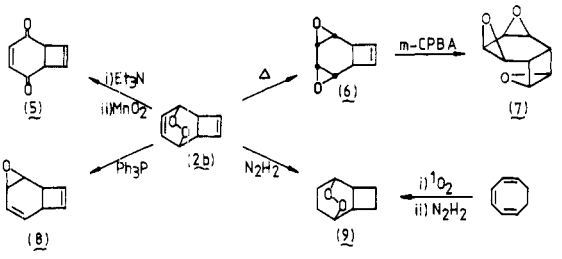
(10) For **7**: ^1H NMR ($CDCl_3$, Me_4Si) δ 2.81 (s, 2 H), 3.13 (m, 2 H), 3.45 (m, 2 H), 4.10 (s, 2 H); IR (KBr) 3000, 2980, 2940, 980, 940, 860 cm^{-1}.

0022-3263/80/1945-5220$01.00/0

Scheme I



Scheme II



respect to the cyclohexane ring, as illustrated in Scheme II. We designate **7** as the syn-anti-syn configuration. This stereochemical course of epoxidation of **6** is indeed surprising since Dreiding models suggest that the syn approach of the mCPBA is sterically less encumbered than the anti approach. It appears that stereoelectronic factors play a role in this unusual epoxidation. On triphenylphosphine deoxygenation of endoperoxide **2b** in $CHCl_3$ at 25 °C the epoxydiene **8** was obtained in 70% yield (mp 81-82 °C, recrystallized from CH_2Cl_2/n-C_6H_{14} mixture after silica gel chromatography at -15 °C).[6,12] Finally, on diimide reduction[11] of endoperoxide **2b** the saturated bicyclic peroxide **9** was obtained in 80% yield (mp 123 °C, recrystallized from n-C_6H_{14}).[6,13] Its structure is confirmed by independent synthesis starting from cyclooctatriene.[14]

The successful singlet oxygenation of the bicyclic valence isomer of cyclooctatetraene opens up new avenues for its synthetic manipulation and utilization. Preliminary efforts reveal that cyclooctatetraene itself can be oxygen difunctionalized via indirect routes to the potentially valuable endoperoxide **2a**.[15]

Acknowledgment is made to the donors of the Petroleum Research Fund (11022-AC-1), administered by the American Chemical Society, the National Science Foundation (Grant No. CHE-78-12621), the National Institutes of Health (Grant No. GM-00141-05 and RR-8102-07), and the Universities of Puerto Rico and Würzburg for generous financial support. We thank BASF for a generous sample of cyclooctatetraene, Professor H. Hopf (Universität Braunschweig) for the ^{13}C NMR spectra, and Dr. K. Peters for the X-ray determination.

Registry No. **1b**, 4011-16-9; **2b**, 6841-69-6; **3**, 4840-84-0; **5**, 54251-47-7; **6**, 75266-45-4; **7**, 75266-46-5; **8**, 75266-47-6; **9**, 249-89-8.

(11) Adam, W.; Eggelte, H. J. *J. Org. Chem.* **1977**, *42*, 3987.

(12) For **8**: ^1H NMR (CCl_4, Me_4Si) δ 2.96-3.37 (m, 4 H), 5.92 (d, 2 H), 6.23 (m, 2 H); IR (CCl_4) 3120, 3080, 3060, 2900, 1580, 1470, 1080, 830 cm^{-1}.

(13) For **9**: ^1H NMR (CCl_4, Me_4Si) δ 2.18 (m, 8 H), 3.03 (m, 2 H), 3.93 (m, 2 H); IR (CCl_4) 2960, 2880, 1475, 1455, 1040, 945 cm^{-1}.

(14) Adam, W.; Erden, I. *Tetrahedron Lett.* **1979**, 2781. The physical constants and spectral data reported for the bicyclic peroxide **9** (structure **3b** in ref 14) are erroneous. We thank Professor H. D. Martin and Mr. M. Kunze of this Institute for calling our attention to this error and for a sample of 1,3,5-cyclooctatriene. Cf. correction in: *Tetrahedron Lett.*, in press.

(15) In our hands the endoperoxides **2b** and **9** were sufficiently stable at room temperature (ca. 20 °C) for routine manipulation; however, in view of the inherent danger of organic peroxides in general, all safety precautions should be taken when working with such compounds.

Supplementary Material Available: Experimental details of these transformations (3 pages). Ordering information is given on any current masthead page.

(16) NIH Career Development Awardee (1975-1980). Send correspondence to the Würzburg address.

Waldemar Adam,*[16] Omar Cueto, Ottorino De Lucchi
Department of Chemistry
University of Puerto Rico
Rio Piedras, Puerto Rico 00931, and
Institute of Organic Chemistry
University of Würzburg
D-8700 Würzburg am Hubland, West Germany
Received June 17, 1980

Palladium-Catalyzed Polyhetero-Claisen Rearrangement

Summary: The S → N allylic rearrangement of *S*-allylthioimidates is performed efficiently by the catalysis of Pd(II) salt to give *N*-allylthioamides (71-100% yields).

Sir: The thioamide group has increasingly been recognized as a useful synthon in organic syntheses.[1] Although the transformation of secondary thioamides to tertiary thioamides is sometimes required in a reaction sequence, a general and satisfactory procedure for such transformation is presently lacking.[2] One apparent possibility is the utilization of the rearrangement of *S*-allylthioimidates to *N*-allylthioamides, but this type of S → N rearrangement is one of the least studied polyhetero-Claisen rearrangements,[3] probably owing to the many possible side reactions (e.g., double bond isomerization, deallylation, etc.).

We have found that Pd(II) catalyzes nicely the S → N allyl group migration of *S*-allylthioimidates and we report the very efficient N-allylation reaction of secondary thioamides.

S-Allylthioimidate (**1**), upon heating in tetralin at 150 °C for 4 h, provided mainly the double bond isomerization product, *S*-propenylthioimidate (**3**, 93%), together with a small amount of the desired rearrangement product, *N*-allyl-*N*-methylthiobenzamide (**2**, 7%) (Scheme I). On the other hand, in the presence of 1 mol% Pd(II) **1** was found to rearrange selectively to give **2** (THF, reflux, 2 h).

Some preliminary results are summarized in Table I, which reveals the efficiency and some interesting features of the reaction. The efficiency of the Pd(II) salt (as $PdCl_2$ or $PdCl_2$-$(PhCN)_2$) is evident by a comparison of entries 1 and 3. Under the same conditions except for the absence of Pd(II), no reaction took place and **1** was recovered completely. Triphenylphosphine retards the reaction (entry 2). Neither Pd(0) (as tetrakis(triphenylphosphine)palladium) nor other metal salts ($NiCl_2$, CuCl, $HgCl_2$)[4] effected the S → N rearrangement. Accompanied by these observations, the regiospecific rearrangements of

(1) (a) Woodward, R. B. *Pure Appl. Chem.* **1968**, *17*, 519; **1971**, *25*, 283; **1973**, *33*, 145. (b) Eschenmoser, A. *Q. Rev., Chem. Soc.* **1970**, *24*, 366. (c) Takano, S.; Hirama, M.; Araki, T.; Ogasawara, K. *J. Am. Chem. Soc.* **1976**, *98*, 7087. (d) Tamaru, Y.; Harada, T.; Yoshida, Z. *Ibid.* **1978**, *100*, 1923; **1979**, *101*, 1316; **1980**, *102*, 2392. (e) Tamaru, Y.; Harada, T.; Iwamoto, H.; Yoshida, Z. *Ibid.* **1978**, *100*, 5221. (f) Tamaru, Y.; Harada, T.; Yoshida, Z. *Tetrahedron Lett.* **1978**, 2167; **1979**, 3525. (g) Tamaru, Y.; Kagotani, M.; Yoshida, Z. *J. Org. Chem.* **1979**, *44*, 2816.

(2) (a) Trost, B. M.; Kunz, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 7152 and references cited therein. (b) Zabicky, J. "The Chemistry of Amide"; Interscience: New York, 1970.

(3) For comprehensive review, see: (a) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1; (b) Bennet, G. B. *Synthesis* **1977**, 589; (c) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227.

0022-3263/80/1945-5221$01.00/0