

**SYNTHESIS OF A VERSATILE FUNCTIONALIZED TETRAQUINANE. CONVENIENT
ACCESS TO 1,3-BISHOMOPENTAPRISMANEDIONE**

Leo A. Paquette,* Koichi Nakamura,¹ and John W. Fischer

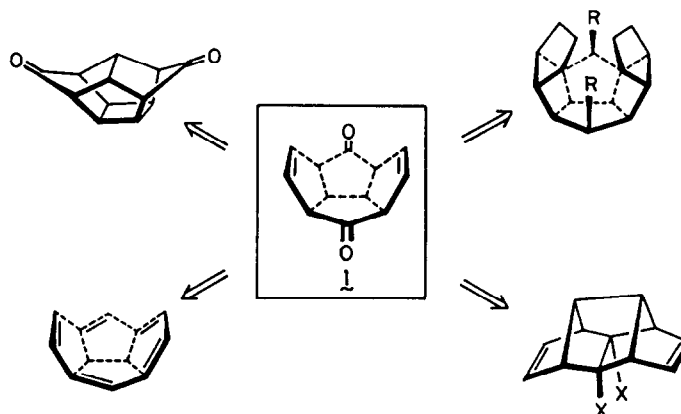
Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Summary: The tetracyclic diene dione **1** has been synthesized by a short oxidative decarboxylation route starting with the domino Diels-Alder adduct **2**. Photocyclization of the bisketal of **1** was used to arrive expediently at 1,3-bishomopentaprismanedione (**7**).

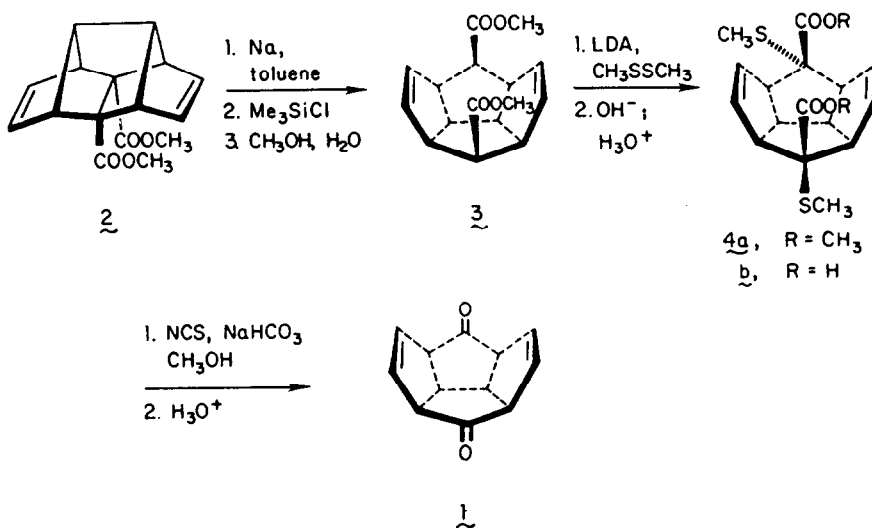
The position of highly condensed, suitably functionalized tetraquinanes as building blocks for the elaboration of complex organic structures would be augmented by the availability of an expedient method for their construction. Only a few serviceable candidates are known,² and their level of substitution is inappropriate.³ This restriction would in large part be overcome if the doubly unsaturated C₁₂-diketone **1** were readily accessible. This symmetrical substance holds considerable promise as a versatile synthetic intermediate for gaining access to previously unavailable 1,3-bishomopentaprismane derivatives, pentagonal dodecahedrane precursors, semi-spheroidal bismethano[10]annulenes, and additional attractive targets (Figure 1). We describe herein an abbreviated route to **1** and demonstrate the ease with which it can be transformed into caged molecules.

Although the direct reductive sulfenylation of **2** to give **4a** could be performed in one operation, it proved more efficient to transform **2** to its dihydro derivative **3** (95%) as previously described.⁴ Condensation of the dianion of **3** with methyl disulfide gave **4a**, with entry of the CH₃S- groups relegated to the exo surface for the usual steric reasons. This crystalline substance, mp 196-197°C, was isolated in 50-55% yield. Since the major by-product was the monosulfenylated diester, which in turn could also be transformed into **4a**, good overall efficiency (90+%) can be realized at this stage. Trost and Tamaru have earlier shown that α -methylthio carboxylic acids can be made to undergo oxidative decarboxylation

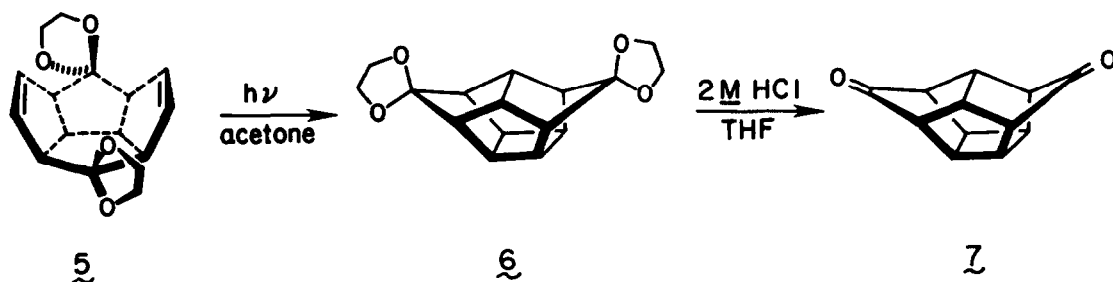
Figure 1



with *N*-chlorosuccinimide in buffered methanol.⁵ To permit implementation of this chemistry, **4a** was hydrolyzed to **4b** (100%) with potassium hydroxide in aqueous methanol. Application of the prescribed conditions to **4b** provided **1** (55%) as a colorless solid, mp 178–180°C dec. The C_{2v} symmetry of **1** follows convincingly from its 300 MHz ^1H NMR [(CDCl₃) δ 5.68 (t, J = 4.0 Hz, 4 H) 3.90 (m, 2 H), 3.63 (dd, J = 2.5, 4.0 Hz, 4 H)] and ^{13}C NMR spectra. The latter consists of only four lines at 214.64(s), 133.52(d), 62.67(d), and 43.06(d) ppm.⁶



Although an X-ray crystal structure analysis of **1** is not currently available, Dreiding models indicate that its pair of double bonds are relatively distant. We envisioned that proximity would need to be enhanced if excited state [2+2] photocycloaddition was to be satisfactorily accomplished. Also, possible undesirable side reactions such as oxa-di- π -methane rearrangements had to be rendered inoperable. It so happens that bisketalization as in **5** (92%, mp 135–136°C) nicely resolves both potential complications. Thus, as the two dioxolane rings in **5** seek to avoid nonbonded steric interaction, the respective tetraquinane carbon atoms move as distant as possible. Linked to this conformational flexing is a concurrent compression of the π bonds. As a result, construction of the 1,3-bishomopentaprismane ring system proceeds smoothly (98.4%) when acetone solutions of **5** are irradiated at 350 nm in a Rayonet reactor.



Caged photoproduct **6**, which forms colorless prisms of mp 118.5–120°C from hexane, is characterized by a six-line ^{13}C NMR spectrum and a definitive proton spectrum consisting of four well-space absorptions: (CDCl_3) δ 3.89 (dd, $J = 4.1, 4.4$ Hz, 4 H), 3.82 (dd, $J = 4.1, 4.4$ Hz, 4 H), 2.80 (m, 6 H), 2.01 (br s, 4 H). Hydrolysis of **6** with 2 M hydrochloric acid in tetrahydrofuran at the reflux temperature proceeds slowly (reaction time 105 h) but efficiently (95.2%) to give **7** (colorless prisms, mp 228.5–230°C): ^1H NMR (300 MHz, CDCl_3) δ 3.26 (br s, 4 H), 3.15 (br s, 2 H), 2.25 (br s, 4 H); ^{13}C NMR (CDCl_3) ppm 210.49, 48.81, 42.30, 41.66.

The straightforward route to **1** described above provides incentive for much additional experimentation. Certainly, this diketone now qualifies as a readily available intermediate. We plan to report on further interesting synthetic applications of **1** at a future date.

Acknowledgment. This work was assisted financially by grants from the National Institutes of Health (AI-11490) and U.S. Army Armament Research and Development Command.

References and Notes

- (1) On sabbatical leave from the Tochigi Research Laboratories of the Kao Corporation (Japan), 1984-85.
- (2) Paquette, L. A. Topics Current Chem. 1979, 79, 41; 1984, 119, 1.
- (3) (a) Paquette, L. A.; Wyvratt, M. J. J. Am. Chem. Soc. 1974, 96, 4671. (b) McNeil, D.; Vogt, B. R.; Sudol, J. J.; Theodoropoulos, S.; Hedaya, E. Ibid. 1974, 96, 4673. (c) Fukunaga, T.; Clement, R. A. J. Org. Chem. 1977, 42, 270.
- (4) Bartetzko, R.; Gleiter, R.; Muthard, J. L.; Paquette, L. A. J. Am. Chem. Soc. 1978, 100, 5589.
- (5) Trost, B. M.; Tamaru, Y. J. Am. Chem. Soc. 1977, 99, 3101.
- (6) Satisfactory combustion analyses have been obtained for all new compounds reported herein.

(Received in USA 10 June 1985)