C=O); nmr τ 2.6–2.9 (4 H, multiplet, aryl H), 6.9–7.3 (2 H, multiplet, benzylic $-CH_2-$), 8.92 (3 H singlet, angular CH_3), 8.93 (3 H, singlet, angular CH_3); mass spectrum (*m/e*) 228 (parent, 65%), 213 (73%), 131 (100%).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.07; H, 8.75.

1-Benzoyloxy-7-methoxy-4a-methyl-2,3,4,4a,9,10-hexahydrophenanthrene (2b).—Following a procedure similar to that for the preparation of **2a**, 5.98 g (0.025 mol) of **1b**[8] was converted into 4.81 g (66%) of **2b**: mp 84–86°; infrared 5.78 μ (enol benzoate C=O); nmr τ 1.8–2.0 (2 H, multiplet, orthobenzoloxy aryl H), 2.4–3.5 (7 H, multiplet, aryl H), 6.24 (3 H, singlet, OCH_3), 8.54 (3 H, singlet, angular CH_3); ultraviolet λ_{max} 285 mμ (log ϵ 3.46), 275 (3.54), 228 (4.36); mass spectrum (*m/e*) 348 (parent 0.5%), 333 (6%), 105 (100%).

Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 79.33; H, 7.04.

cis- **(4b)** and *trans*-**4a,10a-Dimethyl-7-methoxy-3,4,4a,9,10,10a-hexahydro-1(2H)-phenanthrone (5b).**—Following a procedure similar to that for the preparation of **4a** and **5a**, 1.00 g (2.87 mmol) of **2b** was converted into 0.533 g (72%) of a 70:30 mixture of **4b** and **5b**. Crystallization of the mixture from hexane at room temperature yielded 114 mg (16%) of pure **5b**: mp 128–129.5; infrared 5.87 μ (saturated C=O); nmr τ 2.6–2.9 (1 H, multiplet, aryl H), 3.0–3.4 (2 H, multiplet, aryl H), 6.21 (3 H, singlet, OCH_3), 8.92 (3 H, singlet, angular CH_3), 8.93 (3 H, singlet, angular CH_3); mass spectrum (*m/e*) 258 (parent 47%), 243 (100%).

Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.35; H, 8.32.

Upon cooling the hexane solutions to 0° **4b** slowly crystallized. After several crops there was obtained 292 mg (40%) of **4b**: mp 50.5–53.5° (after one recrystallization from hexane); infrared 5.88 μ (s, saturated C=O); nmr τ 2.7–2.9 (1 H, multiplet, aryl H), 3.1–3.5 (2 H, multiplet, aryl H), 6.24 (3 H, singlet, $-OCH_3$), 8.77 (3 H, singlet, angular CH_3), 8.90 (3 H, singlet, angular CH_3); mass spectrum (*m/e*) 258, 243 (100%).

Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.14; H, 8.75.

Registry No.—**2a**, 18968-34-8; **2b**, 18936-36-2; **4a**, 18936-37-3; **4b**, 18936-38-4; **5a**, 18936-39-5; **5b**, 18936-40-8.

The Epoxidation of 3,3,6,6-Tetramethyl-1,4-cyclohexadiene[1]

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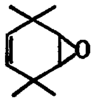
In 1965, we reported the synthesis and some reactions of 3,3,6,6-tetramethyl-1,4-cyclohexadiene (**1**).[2] Our interest in this system and the reports of the unusual reactivity of the structurally similar norbornadiene toward epoxidation[3] stimulated us to investigate the oxidation of **1** with peracetic acid. The recent publication of Berchtold's work on 1,4-cyclohexadiene[4] prompted us to report our findings.

The starting material, **1**, as obtained by the pyrolysis of the diacetate of 2,2,5,5-tetramethylcyclohexane-1,3-diol was contaminated with about 20% *p*-xylene.[2] To obviate the necessity of separating this contaminant from **1** it was determined that *p*-xylene did not react with peracetic acid under the conditions of our experiments. The epoxidation of **1** with peracetic acid in the presence of sodium carbonate[5] resulted in the formation of 2,2,5,5-tetramethyl-7-oxabicyclo[4.1.0]heptane (**2**) in 30% yield and *cis*-2,2,6,6-tetramethyl-4,8-dioxatricyclo[5.1.0.0^{3,5}]octane (**3**) in 11% yield. A gas chromatogram of the crude reaction mixture indicated that these were the only volatile products present and thus **1** upon epoxidation does not yield any products resulting from a skeletal rearrangement. The low yields of the two products were the result of their isolation by preparative gas chromatography rather than the presence of unidentified reaction products.

1



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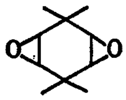

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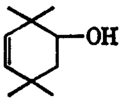

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Monoepoxide **2** was characterized by its elemental analysis, its spectral properties, and its conversion by reduction with lithium aluminum hydride into 3,3,6,6-tetramethylcyclohexen-4-ol (**4**).

In order to place the structural assignment of **2** on firm ground, but with the somewhat unusual lithium aluminum hydride reduction of *exo*-2,3-epoxynorborn-5-ene[3b] in mind, we reduced **2** with lithium aluminum hydride. As in the epoxidation reaction above there was no evidence of a sketetal rearrangement and **4** was obtained in 71% yield. This material was identified by its elemental analysis, its spectral properties, and its conversion into a 3,5-dinitrobenzoate.

Bisepoxide **3** was characterized by its elemental analysis and its infrared and nmr spectra. The *cis* stereochemistry was assigned on the basis of the nmr spectrum and the examination of a molecular model of monoepoxide **2**. The nmr spectrum of **3** (CCl_4) had a singlet at δ 1.08 (6 H), a singlet at 1.22 (6 H), and a singlet at 2.56 (4 H). This spectrum is consistent with a system with four equivalent ring junction protons and a nonequivalent pair of two equivalent methyl groups, that is, the *cis*-bisepoxide. The *trans*-bisepoxide would be expected to have an nmr spectrum that would indicate the equivalence of the 12 methyl protons and the equivalence of the four ring junction protons.

The selective epoxidation of **2** to form **3** can be understood by examination of a molecular model of **2**. The combination of the epoxide ring (with forces carbon atoms 3, 4, 5, and 6 into a plane[6]) and the carbon–carbon double bond (which forces carbon atoms 1, 2, 3, and 6 into a plane) requires that the ring assume a boat conformation. There are two boat conformations possible. In one, **5**, the "flagpole" and "bowsprit" methyl groups are *trans* to the oxide ring and, in the other, **6**, they are *cis* to the oxide ring. Inspection of models of the two conformers shows that in **6** there are two hydrogen–methyl eclipsings and two methyl–

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[1] Taken from the M.S. Thesis of J. T. S., Middlebury College, 1967.

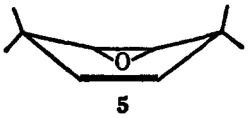
[2] F. W. Grant, R. W. Gleason, and C. H. Bushweller, *J. Org. Chem.*, **30**, 290 (1965).

[3] (a) J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Amer. Chem. Soc.*, **85**, 582 (1963); (b) J. Meinwald, S. S. Labana, L. L. Labana, and G. H. Wahl, *Tetrahedron Lett.*, No. 23, 1789 (1965).

[4] T. W. Craig, G. R. Harvey and G. A. Berchtold, *J. Org. Chem.*, **32**, 3743 (1967). The authors are indebted to Professor Berchtold for a copy of their manuscript and for the nmr spectra of the *cis*- and *trans*-bisepoxide of 1,4-cyclohexadiene and to Dr. Craig for a copy of his thesis.

[5] M. Korach, D. R. Nielsen, and W. H. Rideout, *J. Amer. Chem. Soc.*, **82**, 4328 (1960).

[6] B. Ottar, *Acta Chem. Scand.*, **1**, 283 (1947).



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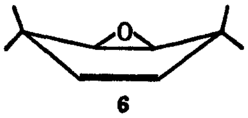

6

oxygen eclipsings that are not present in **5**. It would appear then that **5** would be more stable than **6** by at least 2.6 kcal (the difference in energy between *gauche* butane and that conformer which has two methyl-hydrogen elipsings and one hydrogen–hydrogen eclipsing) and thus would comprise approximately 99% of the mixture of **5** and **6**.[7] Thus the preferred conformation of **2** favors the formation of the *cis*-bisepoxide since in this conformation approach of the epoxidizing species to the carbon–carbon double bond on the side of the molecule *trans* to the epoxide ring is seriously hindered by the "flagpole" and "bowsprit" methyl groups. The preferential formation of the *cis*-bisepoxide should therefore be expected.

Experimental Section[8]

Epoxidation of 3,3,6,6-Tetramethyl-1,4-cyclohexadiene (1).—Following the procedure of Korach[5] 7.85 g of 34% peracetic acid (0.035 mol) which had been saturated with sodium acetate was added dropwise with rapid stirring to a suspension of 5.8 g of sodium carbonate in a solution of 6.0 g (0.035 mol) of **1** and 66.0 g of methylene chloride. The temperature of the reaction mixture was maintained at 23–25° during the course of the addition (0.5 hr) and for a period of 2 hr after the addition was completed during which time the reaction mixture was stirred rapidly. The reaction mixture was cooled to 0° and maintained at that temperature while it was neutralized with 25% sodium hydroxide. The reaction mixture was filtered and the organic layer separated. The aqueous layer was extracted with three 15-ml portions of methylene chloride and the extracts were combined with the original organic layer. After drying ($MgSO_4$) the methylene chloride was separated by distillation and the residue was fractionated using vpc at 133°. In this fashion 1.59 g (30%) of **2** was isolated. It had bp 176–177°; $n^{28}D$ 1.4493; ir (CCl_4) 3080 (=CH), 1650 (C=C), 1250 and 860 (epoxy);[9] nmr ($CDCl_3$) δ 5.07 (m, 2, -**CH**=**CH**-), 2.91 (2, m, epoxy hydrogens), 1.05 (s, 6, 2-CH_3) and 1.1 (s, 6, 2-CH_3).[10]

Anal. Calcd for $C_{10}H_{16}O$: C, 78.84; H, 10.64. Found: C, 78.66; H, 10.62.

Also isolated was 0.60 g (11%) of bisepoxide **3**: mp 83–84°; ir (KBr) 1260, 835 and 820 (epoxy).[9] See discussion for nmr data.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.60. Found: C, 71.22; H, 9.52.

3,3,6,6-Tetramethylcyclohexen-4-ol (4).—A solution of 1.0 g (6.6 mmol) of **2** in 25 ml of anhydrous tetrahydrofuran (THF) was added dropwise with stirring to a suspension of 0.25 g (6.6 mmol) of lithium aluminum hydride in 60 ml of anhydrous THF. After the addition was complete (0.5 hr) the reaction mixture was refluxed for 12 hr. Excess lithium aluminum hydride was destroyed and lithium and aluminum salts were precipitated using the method of Micovic[11] and the supernatent liquid was decanted. The granular inorganic residue was washed with two 10-ml portions of THF and the combined THF solution and washings were dried ($MgSO_4$). The THF was distilled through a semimicro column and the residue was purified by vpc at 133° yielding 0.72 g (71%) of **4**: mp 46–47°; ir (CCl_4) 3700 and 3500 (-OH), 1670 (C=C) and 1040 (CO); nmr ($CDCl_3$) δ 5.22 (s, 2, -**HC**=**CH**-), 3.68 (m, 1, J_{AX} = 7 Hz, J_{BX} = 9 Hz, -C**H**OH), 1.54 (d, 1, J = 9 Hz, -**H**CH-), 1.55 (d, 1, J = 7 Hz, -HC**H**-),[12] 1.06 (s, 3, -CH_3), 1.01 (s, 6, 2-CH_3), and 0.92 (s, 3, -CH_3).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.85; H, 11.78. Found: C, 77.63; H, 11.87.

A 3,5-dinitrobenzoate prepared according to the procedure of Brewster and Ciotti[13] and recrystallized from ethanol–water had mp 103–104°.

Anal. Calcd for $C_{17}H_{23}NO_2$: C, 58.61; H, 5.79; N, 8.04. Found: 58.94; H, 6.10; N, 8.05.

Registry No.—**1**, 2223-54-3; **2**, 19165-53-8; **3**, 19165-54-9; **4**, 19165-55-0.

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[7] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 9.

[8] All melting points and boiling points are uncorrected. The infrared spectra were determined with a Perkin-Elmer Model 137 spectrophotometer. The nmr spectra were determined on a Varian A-60 spectrometer and the data are in parts per million using tetramethylsilane as an internal standard at 0.00 ppm. Gas chromatographic analyses and collections were performed using a 7 ft × 0.25 in. glass column packed with 30% DC 550 on base-washed 60/80 Chromosorb P. The microanalyses were performed by C. F. Geiger, Ontario, Calif.

[9] S. B. Soloway and S. J. Cristol, *J. Org. Chem.*, **25**, 327 (1960).

[10] The olefinic protons and the ring junction protons give rise to what appears to be two triplets centered at the above chemical shifts. A computer analysis of this system obtained through the courtesy of A. H. Turner at the University of Rochester showed $J_{14} = J_{23} = 1.1$ and $J_{13} = J_{24} = 1.2$ Hz.

[11] V. M. Micovic and M. LJ. Mihailovic, *ibid.*, **18**, 1190 (1953).

[12] The coupling constant for the two methylene protons is apparently nearly zero.

[13] J. H. Brewster and C. J. Ciotti, *J. Amer. Chem. Soc.*, **77**, 6214 (1955).

Clemmensen Reduction of 2,2,4,4,6,6-Hexamethyl-1,3,5-cyclohexanetrione. A Reinvestigation

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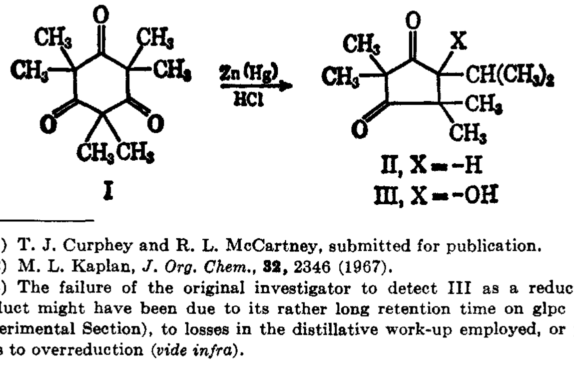
In the course of an investigation on the electrochemical reduction of 1,3-diketones,[1] we had occasion to repeat the recently described[2] Clemmensen reduction of 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetrione (I). Because our results differ from those previously reported in a manner having some mechanistic significance, we wish to report them at this time.

Reduction of I by amalgamated zinc in a two-phase toluene–hydrochloric acid system was reported to give the rearranged diketone II as the sole major product.[2] In our hands repetition of this reduction as originally described led to a crude reaction mixture, glpc analysis of which showed the presence of not one, but *two* major products, present in approximately equal amounts. Samples of the two products were readily isolated from the mixture by preparative glpc. The physical and spectroscopic properties of one of the products agreed with those described[2] for diketone II. The second product was a white crystalline solid to which we have assigned structure III.[3] The infrared spectrum of III



I

II, X = -H

III, X = -OH

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[1] T. J. Curphey and R. L. McCartney, submitted for publication.

[2] M. L. Kaplan, *J. Org. Chem.*, **32**, 2346 (1967).

[3] The failure of the original investigator to detect III as a reduction product might have been due to its rather long retention time on glpc (see Experimental Section), to losses in the distillative work-up employed, or perhaps to overreduction (*vide infra*).