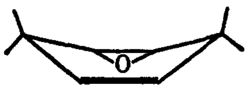
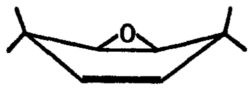


5



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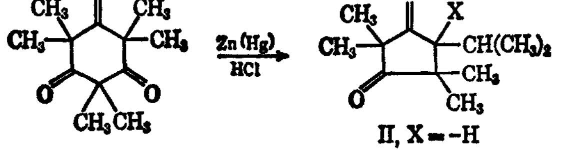
In the course of an investigation on the electrochemical reduction of 1,3-diketones,[1] we had occasion to repeat the recently described[2] Clemmensen reduction of 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetrione (I). Because our results differ from those previously reported in a manner having some mechanistic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

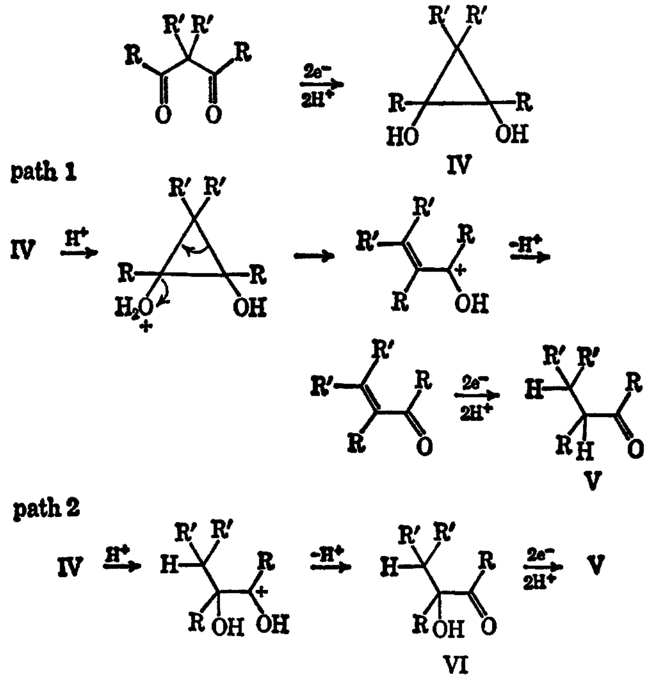
[3] The failure of the original investigator to detect III as a reduction product might have been due to its rather long retention time on glpc (see Experimental Section), to losses in the distillative work-up employed, or perhaps to overreduction (*vide infra*).

was similar to that of II but showed an additional sharp band at 3480 cm^{-1} attributed to –OH stretch. The 100-MHz nmr spectrum of III in benzene solution showed a singlet at δ 3.03 for the –OH group, a septet (after time-averaging for 31 scans) at δ 1.67 (J = 7 Hz) for the methine hydrogen, four singlets at δ 1.14, 1.12, 1.01, and 0.94 for the methyl groups attached to the ring, and two doublets (J = 7 Hz) at δ 0.93 and 0.73 for the two nonequivalent isopropyl methyls. Elemental analysis agreed with the assignment of structure III to this product.

The genetic relationship between II and III was explored by repeating the reduction with periodic glpc examination of aliquots of the reaction mixture. Table I shows the results of this experiment. As expected from the data shown in Table I, a reduction terminated after 22 hr gave a mixture from which II and III were isolated in yields (based on starting material taken) of 24 and 26%, respectively. Likewise, prolongation of the reduction period to 70 hr gave a 49% yield of II. The implication of these experiments, that III is the precursor of II, was further strengthened by subjecting III to the conditions of the Clemmensen reduction, whereupon II was isolated in 41% yield.

The mechanism of the abnormal Clemmensen reduction of certain 1,3-diketones has been the object of much recent investigation and discussion, principally by two groups of workers.[4–6] Both groups accepted the suggestion of Staschewski[4] that the first step in the reaction of such ketones is the formation of cyclopropanediol IV by an intramolecular pinacol reduction, but they initially differed on the subsequent fate of IV. On the one hand, Davis and coworkers[5a,c] adopted Staschewski's original suggestion that IV undergoes an acid-catalyzed rearrangement (Scheme I, path 1) to an unsaturated ketone,[7] the latter then being further reduced to the rearranged ketone V. Such a scheme was advanced by Kaplan[2] to rationalize the formation of II from I. On the other hand, Wenkert and Kariv[6] suggested (Scheme I, path 2) that protolysis of IV leads not to an unsaturated ketone, but to ketol VI, which is then further reduced to V. Clearly our isolation of ketol III from the reduction of I supports the Wenkert mechanism for such reductions. The fact that apparently in no case has an unsaturated ketone been detected as an intermediate in the abnormal Clemmensen reduction of a 1,3-diketone and that, where a careful search has been made, ketol intermediates were isolated,[5b,6] often as major products, strongly suggests that there is currently no basis for invoking the intermediacy, however mechanistically plausible, of unsaturated ketones in such reductions. Recent work by Davis[5b] has apparently led him to the same conclusion.

SCHEME I



Experimental Section[8]

Clemmensen Reduction of 2,2,4,4,6,6-Hexamethyl-1,3,5-cyclohexanetrione.—A mixture of 12 g of amalgamated zinc,[2] 8 ml of water, 18 ml of concentrated hydrochloric acid, 10 ml of toluene and 2.1 g (0.01 mol) of triketone was refluxed with magnetic stirring. At periodic intervals 8-ml portions of hydrochloric acid (at 5, 8, 22, 30, 32, 44, and 55 hr) and 4-g portions of amalgamated zinc (at 24, 30, 45, and 60 hr) were added. During the course of the reaction aliquots of the toluene layer were withdrawn, worked up, and analyzed on a 6 ft × 0.25 in. column of 20% XF-1150 on acid-washed silanized Chromosorb W operated at 165° and a helium flow rate of 80 ml/min. Under these conditions the retention time of I was 11 min, of II 6 min, and of III 15 min.[3] The results of these analyses are presented in Table I.

TABLE I

PRODUCT COMPOSITION DURING THE CLEMMENSEN REDUCTION OF I

Time, hr	Composition, %[a]		
	I	II	III
4	89	3	8
9	78	8	14
22	35	30	35
29	19	48	33
48	4	80	16
69	1	88	11

[a] Expressed as per cent of the total peak area for I + II + III. No correction for detector sensitivity was applied.

After 70 hr the total reaction mixture was worked up, the organic extract concentrated at the water pump, and the residue distilled under high vacuum. The distillate was recrystallized from pentane at −78° to give 0.96 g (49%) of **2,2,4,4-tetramethyl-5-isopropyl-1,3-cyclopentanedione** (II), mp 29.5–30.4° (lit.[2] mp 30°). The ir and nmr spectra of this material were as previously described[2] with the exception that on our ir instrument

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(4) D. Staschewski, *Angew. Chem.*, **71**, 726 (1959).

(5) (a) N. J. Cusack and B. R. Davis, *Chem. Ind.* (London), 1426 (1964); (b) K. M. Baker and B. R. Davis, *ibid.*, 768 (1966); (c) N. J. Cusack and B. R. Davis, *J. Org. Chem.*, **30**, 2062 (1965).

(6) E. Wenkert and E. Kariv, *Chem. Commun.*, 570 (1965).

(7) This rearrangement was postulated to involve the intermediacy of cyclopropyl cations, but recent work on the chemistry of cyclopropanols [see C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968)] favors revision to the concerted ring opening as depicted.

(8) Melting points were taken using Anschütz thermometers fully immersed in a stirred oil bath. Infrared spectra were measured on dilute solutions in carbon tetrachloride using a Beckman IR-5A spectrophotometer. The nmr spectra were measured with Varian Associates Models HA-100 and A-60 spectrometers on solutions containing internal tetramethylsilane reference. A Varian C-1024 time-averaging computer was employed in conjunction with the 100-MHz spectrometer. Gas-liquid partition chromatography (glpc) was performed on a Wilkens Aerograph Model A-90-P3. All reaction mixtures were worked up by extracting the aqueous phase with ether, washing the combined organic phases with saturated sodium bicarbonate and sodium chloride solutions, and drying the extract over magnesium sulfate.

the carbonyl bands fell at 1720 (s) and 1760 cm^{-1} (w) instead of at 1745 and 1780 cm^{-1}. When the reaction was terminated after refluxing for only 22 hr and the total organic extract (after concentration at the water pump) chromatographed on a 20 ft × $\frac{3}{8}$ in. column of 30% SE-30 at 260° and a flow rate of 80 ml/min, there was obtained 0.47 g (24%) of II and 0.54 g (26%) of III. The sample of **2,2,4,4-tetramethyl-5-hydroxy-5-isopropyl-1,3-cyclopentanedione** (III) thus obtained had mp 37.6–38.0°, absorbed in the ir at 1720 (s), 1760 (w), and 3480 cm^{-1} (m), and in the nmr (see text for analysis) at δ 3.03 (singlet, 1 H), 1.67 (septet, J = 7 Hz, 1 H), and 0.7–1.2 (multiplet, 18 H).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.01; H, 9.68.

Clemmensen Reduction of III.—A 0.230-g sample of III was subjected to the reduction procedure described above for a reaction time of 43 hr. Glpc analysis of the mixture at this time showed approximately 7% unreacted III and 62% II. Separation and purification by preparative glpc gave 0.078 g of II (41% yield), mp 29.4–30.2°, identical in all respects (ir, nmr, and mixture melting point) with the material prepared directly from I.

Registry No.—I, 778-18-7; III, 19165-42-5.

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A New Spirocyclohexenedione System

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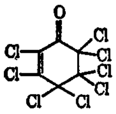
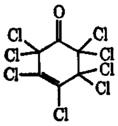
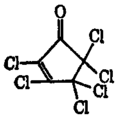
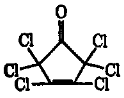
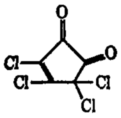
Received July 1, 1968

In the course of an investigation on photodecomposition products of pentachlorophenol,[1] a new spirocyclohexenedione compound (1) was found to form from pyrocatechol by the action of chlorine.

According to Zincke and Küster,[2] pyrocatechol reacts with chlorine in acetic acid to produce tetrachloropyrocatechol. However, it was found that further introduction of chlorine at higher temperature produced new light yellow crystals having the composition $C_{12}Cl_8O_4 \cdot H_2O$ (hydrate) in an 80% yield. Chemical and spectral evidence showed that this was spiro-[2′,3′,4,5,6,6′,6′,7-octachloro-1,3-benzodioxole-2,1′-[2]-cyclohexene]-4′,5′-dione hydrate (1). Mass spectrum of hydrate 1 had a molecular peak at m/e 488 (M^+, 8Cl, as an anhydrous form). Ultraviolet and infrared spectra showed the presence of an α,β-unsaturated ketone group (see Table I) and a phenoxyl nucleus. Dehydration of 1 yielded a yellow colored anhydrous substance, $C_{12}Cl_8O_4$ (2), showing spectral bands of an unsaturated 1,2-diketone.[3] The anhydrous substance lost its color in air owing presumably to the conversion of the 1,2-diketone system by the hydration into the ketone system. The infrared spectra of 1 and 2 agreed with this view. When 1 was dissolved in 75% acetic acid and the solution was poured into water, a colorless dihydrate (3) was precipitated. The infrared spectrum showed no carbonyl absorption and the ultraviolet spectrum at λ_{max} 234 mμ was compatible with a monoene structure.

TABLE I

PRINCIPAL BANDS IN ULTRAVIOLET AND INFRARED SPECTRA OF DERIVATIVES

Compd	λ_{max}, mμ (ϵ)	Solvent	ν_{max}, cm^{-1}
1	261 (17,000)	$CHCl_3$	1,730[a]
 [d]	267–268 (10,500)	C_6H_{12}	1,745[b]
 [d]	235–237 (9,000)	C_6H_{12}	1,779[b]
 [e]	259 (10,000)	95% C_2H_5OH	1,739[c]
 [e]	223 (10,000)	95% C_2H_5OH	1,776[c]
 [f]	226 (12,300) 283 (7,840)	C_6H_{14}	1,795 1,748[b]

[a] KBr disk. [b] CCl_4 solution. [c] $CHCl_3$ solution. [d] L. Denivelle and R. Fort, *C. R. Acad. Sci., Paris,* **242,** 2359 (1956). [e] See ref 7. [f] R. M. Scribner, *J. Org. Chem.,* **30,** 3657 (1965).

Reaction of 1 with o-phenylenediamine to form dihydrophenazine 4 confirmed the potential 1,2-diketone system. Acetylation of 1 gave a colorless spiro acetyl ketal (5). On reduction, 1 afforded a phenol derivative which gave a triacetate. The reductive acetylation of 1 afforded the same compound. These compounds were identical with a quinol[4] and the acetate[4] derived from 3,4,6-trichloro-5-(2,3,4,5-tetrachloro-6-hydroxyphenoxy)-1,2-benzoquinone, respectively.[1,5] Chlorination of this benzoquinone gave 1 in good yield. Alkaline hydrolysis of 1 yielded a monobasic acid (6) which was proved to be a product of the benzylic acid rearrangement (Scheme I). In infrared spectrum, the carbonyl band of 6 was similar to that of 1-hydroxy-2,3,4,4,5,5-hexachloro-2-cyclohexene-1-carboxylic acid.[2]

Hexachloro-3-cyclohexene-1,2-dione (8),[2] the anhydrous chlorination product of pyrocatechol, gave, on the benzylic acid rearrangement, 1-hydroxy-2,3,4,4,5,5-hexachloro-2-cyclohexene-1-carboxylic acid which on decarboxylation gave rise to hexachlorocyclopentenone. The Raman spectra[6] as well as physical[7] and chemical[8] properties of this cyclopentenone furnished its assigned structure. The yellow cyclohexenedione (8) gave, however, readily a colorless monohydrate (9), the

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(1) M. Kuwahara, N. Kato, and K. Munakata, *Agr. Biol. Chem.* (Tokyo), **29,** 880 (1965); **30,** 232, 239 (1966).

(2) T. Zincke and F. Küster, *Ber.,* **21,** 2719 (1888); W. Eller and V. Lorenz, *ibid.,* **58,** 494 (1925).

(3) N. B. Haynes, D. Redmore, and C. J. Timmons, *J. Chem. Soc.,* 2420 (1963).

(4) C. L. Jackson and G. L. Kelley, *Amer. Chem. J.,* **47,** 197 (1912).

(5) C. L. Jackson and P. W. Carleton, *ibid.,* **39,** 493 (1908).

(6) H. V. Brederode, H. Gerding, and H. J. Prins, *Rec. Trav. Chim. Pays-Bas,* **65,** 174 (1946).

(7) E. T. McBee, D. K. Smith, and H. E. Ungnade, *J. Amer. Chem. Soc.,* **77,** 559 (1955).

(8) J. S. Newcomer and E. T. McBee, *ibid.,* **71,** 946 (1949).