analysis showed approximately 40% conversion of **1** to **5**.[8] After concentration a representative sample, 0.200 g, was spotted on a Kontes K-416000 Chromaflex tlc plate coated with silica gel PF-254 and developed with a 4:1 solution of pentane–ethyl ether to yield three clear spots (**1**, **5**, and **6**) with R_f values of 0.54, 0.45, ad 0.81, respectively. Structures **1** and **6** were proved by isolation of these materials from the tlc plate and comparison (ir, nmr, tlc, and mass spectra) with authentic materials.

1,2,4,10,10-Pentachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene (5).—This material, recovered from the tlc plate, slowly crystallized on standing to give mp 204-207° dec, sealed tube; uv max (cyclohexane) 219 nm (ϵ 2850); ir (CCl_4) 6.30 μ (ClC=CH), 11.73 μ (epoxide); nmr ($CDCl_3$) δ 6.04 (s, 1, H_x), 3.46 (m, 1, H_n), 3.13 (m, 2, H_m), 2.93 (m, 3, H_l), 1.81 (t of d, 1, J = 1.7, 10.0 Hz, H_b), and 0.99 (d, 1, J = 10.0 Hz, H_a); mass spectrum (70 eV), m/e (rel intensity) parent 344 (6.2) five chlorine pattern, P − Cl 309 (49.4) four chlorine pattern, base P − C_5H_6ClO 227 (78.0) four chlorine pattern, 82 (63.0), and 81 (75.2). The fragmentation pattern of photoproduct **5** is remarkably similar to that of **1** as seen by the alignment of their molecular ions.

Anal. Calcd for $C_{12}H_9Cl_5O$: C, 41.60; H, 2.62; Cl, 51.18. Found: C, 41.44; H, 2.89; Cl, 51.40.

Registry No.—**1**, 72-20-8; **2**, 33487-97-7; **5**, 33487-96-6.

Acknowledgment.—This investigation was supported in part by the Celanese Corp., Standard Oil of Ohio, and the Purdue Research Foundation, and by generous samples of Endrin from the Shell Development Co.

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[8] An initial solution containing 8.5 g of Endrin gave over 95% conversion of **1** to **5** in 4 hr.

Oxidation of Tetramethyl-1,3-cyclobutanedione under Baeyer-Villiger Conditions

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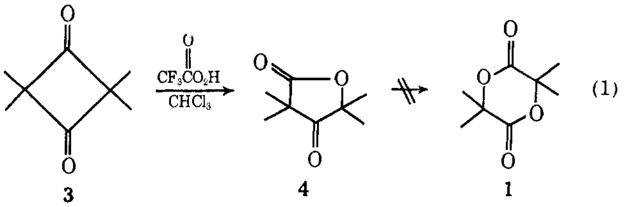
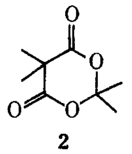
Received September 14, 1971

As part of a study on the acyloin reaction of lactones, we required large quantities of dilactones **1** and **2**. A scan of the literature revealed only one laboratory synthesis of **1**,[1] a vacuum pyrolysis of α-hydroxyisobutyric acid. The reported yield of **1** was 12% (10% in our hands).

It occurred to us that we might be able to synthesize **1** and/or **2** as a separable mixture by treating tetramethyl-1,3-cyclobutanedione (**3**) with 2 equiv of peracid (eq 1).



3 **4** **1**

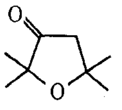


2

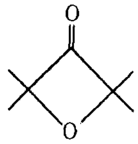
When this reaction was attempted using either monopermaleic acid[2a] or trifluoroperacetic acid[2b] in $CHCl_3$, only one product was formed. It was identified by its physical and spectral properties as 3,3,5,5-tetramethyl-2,4-furandione (**4**). When only 1 mol of peracid was used, **4** could be obtained in yields ranging from 95 to 75% depending on the scale of the reaction (0.1-to 1 mol).

Ketolactone **4** could not be further oxidized using either monopermaleic acid or trifluoroperacetic acid in chloroform even if the mixtures were heated for several days. In most cases good yields of **4** could be recovered. When the oxidation was run using monopermaleic acid in concentrated H_2SO_4–$CHCl_3$ (1:3), no oxidation products were observed but only 35% of **4** was recoverable. No attempt was made to isolate acidic products since if **1** were formed and subsequently hydrolyzed, α-hydroxyisobutyric acid would be formed and it, as noted, cannot be readily converted to **1**.

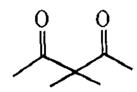
As part of the same project, we also found we were not able to oxidize 2,2,5,5-tetramethyl-3-furanone (**5a**)[3] by any of the above procedures.



5a



5b



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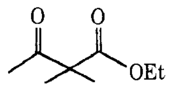

7

Boeseken and Jacobs[4] have shown that 2,2-dialkyl-1,3-dicarbonyl compounds **6** and **7** fail to undergo Baeyer-Villiger reaction. They speculated that the ketone carbonyls are too hindered to permit attack of the peracid. While this explanation might account for the lack of reaction of **4** and **5a**, it does not account for the facile reaction of **3** or **5b**[5] under similar conditions since their carbonyls are equally hindered to attack by the peracid. It seems apparent, however, that if the peracid can add to the carbonyl group of **3**, relief of ring strain will be a driving force for product formation.

While we do not intend to pursue this approach to **1**, the Baeyer-Villiger reaction on tetramethylcyclobutanedione appears to be an excellent and simple procedure for the synthesis of tetramethyltetronic acid (**4**), and probably of the other tetraalkylated derivatives of tetraonic acid, an important molecule in sugar chemistry.

Experimental Section

Melting points were taken on a Mel-temp apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 337 spectrometer; nmr spectra were recorded on a Varian A-60 spectrometer using TMS as an internal standard. Mass spectra were obtained on a Hitachi RMU6D mass spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

3,3,5,5-Tetramethyl-2,4-furandione (4) from 3.—Maleic anhydride (1.0 mol) is added carefully to a stirred mixture of 34 g of 98% hydrogen peroxide (1 mol + 10%) in 760 ml of $CHCl_3$. The mixture is warmed gently until the maleic anhydride is all

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[1] A. Golomb and P. D. Ritchie, *J. Chem. Soc.*, 838 (1962).

[2] (a) R. H. White and W. D. Emmons, *Tetrahedron*, **17**, 31 (1962); (b) W. F. Soger and A. Ruckworth, *J. Amer. Chem. Soc.*, **77**, 188 (1955).

[3] G. Dupont, *Ann. Chim Phys.*, **30**, 485 (1915).

[4] J. A. J. Boeseken and J. Jacobs, *Recl. Trav. Chim. Pays-Bas*, **55**, 804 (1936).

[5] J. K. Crandell and W. H. Machleder, *Tetrahedron Lett.*, 6037 (1966).

reacted. Dione **3**, 143.7 g (1.01 mol) in 250 ml of $CHCl_3$, is added to the mixture at such a rate as to maintain a gentle reflux. After allowing the mixture to cool to room temperature, the $CHCl_3$ is washed with saturated K_2CO_3 and H_2O, dried $CaCl_2$, filtered, and evaporated. The crude white solid residue is recrystallized from ether–petroleum ether giving 120.1 g (76.5% yield) of **4**: mp 37.5°; ir (CCl_4) 1796, 1750, 1375, 1360 cm^{-1}; nmr $(^{TMS}_{CCl_4})$ δ 1.29 (s, 6), 1.50 (s, 6); mass spectra (70 eV, rel intensity) *m/e* 156 (m$^+$, 4), 141 (2), 128 (20), 113 (20), 71 (10), 70 (100), 43 (23), 42 (62), 41 (25), 39 (51), metastable peak 25.4.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.79; H, 7.89.

Registry No.—**3**, 933-52-8; **4**, 4387-74-0.

Sigmatropic Chlorine Migration in 5-Chloro-5*H*-dibenzo[*a,d*]cycloheptenes

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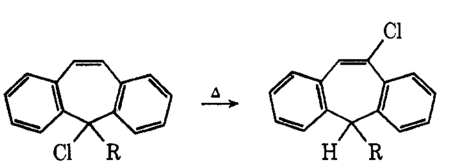
The scope of the thermal chlorine migration exemplified by the isomerization[1] of 5,5-dichloro-5*H*-dibenzo[*a,d*]cycloheptene (**1a**) to the 5,10 isomer **2a** has been examined. The intent was to uncover the driving force for the migration, since it was not clear why it should occur. When there is one hydrogen and one chlorine atom at position 5, no rearranged product is formed; only decomposition occurs upon heating. When one substituent is chlorine and the other is phenyl (**1c**) or 1-naphthyl (**1d**), the chlorine atom migrates to position 10 affording **2c** and **2d**, respectively. Thus, two large groups on carbon 5 appear necessary for migration to occur. This suggests that relief of crowding between the equatorial substituent on carbon 5 and the peri hydrogen atoms may be the reason for migration, since the rearranged product now has the smaller hydrogen atom in the sterically unfavorable equatorial position. Molecular models of these compounds confirm the presence of the suggested steric interactions.

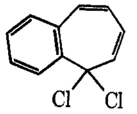


1 **2**

a, R = Cl
b, R = H
c, R = phenyl
d, R = 1-naphthyl

A comparison of the nmr spectra of the unrearranged (**1**) and rearranged (**2**) chlorides supports the hypothesis that crowding is relieved by migration. All chlorides with two large groups at carbon 5 (**1a**, **1c**, **1d**) have a two-proton multiplet downfield (τ 1.3–1.8) from the other aromatic protons. This absorption can be assigned to the protons on carbon 4 and carbon 6, which are very close to the equatorial substituent at position 5. This downfield shift of the aromatic protons is analogous to that observed for the peri hydrogen atom in 1-substituted naphthalenes.[2] When migration occurs, leaving a hydrogen atom to occupy the equatorial position (**2a**, **2c**, **2d**), this absorption disappears. The lowest resonance in these compounds is a one-proton multiplet at τ 2.0–2.2, which is assigned to the aromatic hydrogen peri to the vinyl chlorine atom.

Two gem-dichlorides void of the suggested steric interaction were pyrolyzed to see if migration would occur. Neither 5,5-dichloro-5*H*-benzocycloheptene (**3**) nor chlorotropylium chloride (**4**) gave thermally rearranged chlorides. Decomposition occurred in a manner very similar to the behavior of 5-chloro-5*H*-dibenzo[*a,d*]cycloheptene (**1b**), and led to unidentifiable material.



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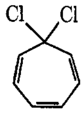
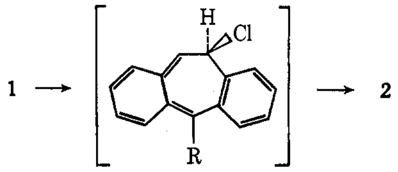


4

The original reaction path suggested[1] for this chlorine migration involved ionic intermediates. A better proposal appears to be a concerted 1,5-sigmatropic chlorine migration (**1** → **5**), followed by a 1,5-hydrogen shift (**5** → **2**). Both processes can occur in the allowed suprafacial manner in this ring system.



5

Experimental Section[3]

5-Chloro-5-phenyl-5*H*-dibenzo[*a,d*]cycloheptene (**1c**).—A solution of 8.2 g (0.029 mol) of 5-hydroxy-5-phenyl-5*H*-dibenzo[*a,d*]cycloheptene[4] in 25 ml of thionyl chloride was heated at reflux for 1 hr. The solvent was removed leaving a white solid, mp 191–193°. An analytical sample was prepared by repeated recrystallization from ligroin (bp 63–75°): mp 201–203° dec (depends upon rate of heating); nmr τ 3.40 (s, 2, vinyl), 2.5–3.4 (m, 8, aromatic), 1.5–1.7 (m, 2, aromatic at C-4 and C-6).

Anal. Calcd for $C_{21}H_{15}Cl$: C, 83.3; H, 5.0; Cl, 11.7. Found: C, 83.3; H, 5.3; Cl, 11.4.

10-Chloro-5-phenyl-5*H*-dibenzo[*a,d*]cycloheptene (**2c**).—The crude chloride **1c** (from 10 g of the alcohol) was heated at 205° for 1 hr and recrystallized from ligroin (bp 63–75°): 6.5 g (74%); mp 114–116°; nmr τ 4.70 (s, 1, benzylic), 2.5–3.5 (m, 12, aromatic), 2.0–2.2 (m, 1, aromatic peri to Cl).

Anal. Calcd for $C_{21}H_{15}Cl$: C, 83.3; H, 5.0; Cl, 11.7. Found: C, 83.0; H, 4.8; Cl, 11.4.

5-Chloro-5-(1-naphthyl)-5*H*-dibenzo[*a,d*]cycloheptene (**1d**).—A solution of 10 g (0.030 mol) of 5-hydroxy-5-(1-naphthyl)-5*H*-dibenzo[*a,d*]cycloheptene[5] in 50 ml of thionyl chloride was heated at reflux for 1 hr and concentrated, and the solid was recrystallized from methylcyclohexane: 2.75 g (25%); mp 171–172°; nmr τ 2.2–3.6 (m, 15, aromatic and vinyl), 1.3–1.6 (m, 2, aromatic at C-4 and C-6).

10-Chloro-5-(1-naphthyl)-5*H*-dibenzo[*a,d*]cycloheptene (**2d**).—A solution of 1.0 g (0.0028 mol) of **1d** in 20 ml of *o*-dichlorobenzene was heated at reflux for 45 min, concentrated, and chromatographed on Florisil. The benzene–ligroin (1:1) fraction gave a white solid, which was recrystallized from ligroin: 0.57 g

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[1] J. J. Looker, *J. Org. Chem.*, **31**, 3599 (1966).

[2] V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

[3] Melting points and boiling points are uncorrected. The nmr spectra were measured on a Varian Associates A-60 instrument in deuteriochloroform, with TMS as an internal standard.

[4] W. Treibs and H. Klinkhammer, *Chem. Ber.*, **84**, 671 (1951).

[5] J. J. Looker, *J. Org. Chem.*, **36**, 1045 (1971).