**General Procedure for the $BBr_3$-Catalyzed Rearrangement of Cyclopropanecarboxylates.** A solution of cyclopropanecarboxylate (1 equiv, 0.1–0.4 M) in $CH_2Cl_2$ was added dropwise to a stirred solution of $BBr_3$ (1 M in $CH_2Cl_2$, 0.5 equiv), in $CH_2Cl_2$ at −78 °C under Ar. The mixture was maintained at −78 °C for 20 min and then warmed to rt for 3 h. After the mixture was quenched with alcohol or water, water was added and the mixture was extracted twice with ether. The combined organic layers were extracted with water and saturated NaCl solution, dried ($Na_2SO_4$), and concentrated. All proudcts were purified by column chromatography on silica using ether–petroleum ether as eluant in the ratio specified in parenthesis.

**Methyl 2-Ethylidene-4-oxobutanoate (5):**[9] **3** (0.17 g, 3.0 mmol), $H_2O$ quench (1:4); yield 0.053 g (48%); IR (neat) 2970, 2920, 2910, 1770, 1710, 1650 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 9.62 (t, $J$ = 1.6 Hz, 1 H), 7.14 (q, $J$ = 7.2 Hz, 1 H), 3.73 (s, 3 H), 3.42 (s, 2 H), 1.79 (d, $J$ = 7.2 Hz, 3 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 198.2, 167.1, 142.0, 124.7, 52.1, 41.5, 14.8.

**3-Ethylidene-2-oxo-5-phenyl-4,5-dihydrofuran (13a) and 2-oxo-5-phenyl-3-vinyl-4,5-dihydrofuran (13b):** **11** (0.90 g, 3.7 mmol), stirred at room temperature for 2 h and then quenched with ethanol at −78 °C (3:17) combined yield 0.26 g (37%, 1:1 partially separable mixture). **13a**: IR (neat) 1750, 1675 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.42–7.24 (m, 5 H), 6.91–6.81 (m, 1 H), 5.52 (dd, $J$ = 8.3, 6.4 Hz, 1 H), 3.31 (dddq, $J$ = 17.0, 8.3, 2.6, 1.9 Hz, 1 H), 2.76 (dddq, $J$ = 17.0, 6.4, 2.9, 1.9 Hz, 1 H), 1.84 (dt, $J$ = 7.0, 1.9 Hz, 3 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 170.5, 140.4, 136.1, 128.7, 128.3, 126.8, 125.2, 77.9, 34.0, 15.9. **13b**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.49–7.25 (m, 5 H), 5.99 (ddd, $J$ = 16.9, 10.4, 6.3 Hz, 1 H), 5.41 (dd, $J$ = 10.6, 5.7 Hz, 1 H), 5.29 (d, $J$ = 10.4 Hz, 1 H), 5.24 (d, $J$ = 16.9 Hz, 1 H), 3.50 (ddd, $J$ = 13.3, 8.3, 5.7 Hz, 1 H), 2.83 (m, 1 H), 2.13 (apparent q, $J$ = 11.5 Hz, 1 H). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.53; H, 6.45.

**General Procedure for the $VOCl_2(OEt)$-Induced Reactions of Cyclopropanecarboxylates.** A solution of the vinylcyclopropane (1 equiv, 0.05–0.5 M) in $CH_2Cl_2$ was added dropwise to a stirred solution of $VOCl_2(OEt)$ (2 equiv, 0.1–1 M) in $CH_2Cl_2$ at 0 °C under stirring. After the solution was stirred for a further 5 min, water was added and the mixture was extracted (2×) with ether. The combined organic layers were washed with water and saturated NaCl solution, dried ($Na_2SO_4$), and concentrated. The residue was then purified by chromatography on silica with the specified solvent.

**5-Ethoxy-3-ethylidene-2-oxo-4,5-dihydrofuran dimer (14a):** **6a** (0.21 g, 1 mmol), yield 0.07 g (45%) (ether); IR ($CCl_4$) 1770, 1590 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 6.66–6.63 (m, 2 H), 5.54 (dd, $J$ = 6.4, 2.0 Hz, 2 H), 3.49 (dq, $J$ = 9.4, 7.1 Hz, 2 H), 3.36 (dq, $J$ = 9.4, 7.1 Hz, 2 H), 2.98 (br d, $J$ = 17.4 Hz, 2 H), 2.66 (br d, $J$ = 17.4 Hz, 2 H), 2.33 (m, 4 H), 1.20 (t, $J$ = 7.1 Hz, 6 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 169.4, 138.5, 126.4, 101.1, 65.2, 32.8, 28.7, 14.9; MS $m/e$ (rel intensity) 311 ($(M + H)^+$, 22), 162 (30), 110 (35), 91 (32), 53 (100). Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.14. Found: C, 62.00; H, 7.18.

**5-Butoxy-3-ethylidene-2-oxo-4,5-dihydrofuran dimer (14b):** **6b** (0.24 g, 1 mmol), yield 0.09 g (51%), ether/petroleum ether (3:1); IR ($CCl_4$) 1750, 1670 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 6.75–6.51 (m, 2 H), 5.52 (dd, $J$ = 6.4, 2.2 Hz, 2 H), 3.82 (dt, $J$ = 9.5, 6.8 Hz, 2 H), 3.52 (dt, $J$ = 9.5, 6.8 Hz, 2 H), 2.98 (br d, $J$ = 17.4 Hz, 2 H), 2.66 (br d, $J$ = 17.4 Hz, 2 H), 2.33 (m, 4 H), 1.56 (quintet, $J$ = 7.1 Hz, 4 H), 1.35 (sextet, $J$ = 7.1 Hz, 4 H), 0.88 (t, $J$ = 7.2 Hz, 6 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 169.4, 138.5, 126.5, 101.4, 69.5, 32.8, 31.4, 28.7, 19.1, 13.8; MS $m/e$ (rel intensity) 366 ($M^+$, 1), 219 (60), 190 (25), 162 (70), 110 (100); HRMS $m/e$ calcd for $C_{20}H_{30}O_6$ 366.2042, found 366.2031. Anal. Calcd for $C_{20}H_{30}O_6$: C, 65.55; H, 8.25. Found: C, 65.34; H, 8.21.

**(*E*,*E*)-3,8-Bis(methoxycarbonyl)deca-3,7-dienedial (15):** **3** (0.26 g, 1.5 mmol), yield 0.13 g (57%), ether–petroleum ether (1:1); mp 61–62 °C; IR ($CCl_4$) 2970, 2920, 2860, 1710, 1600 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 9.61 (s, 2 H), 6.95 (br t, $J$ = 7.3 Hz, 2 H), 3.71 (s, 6 H), 3.41 (s, 4 H), 2.26 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 197.9, 166.9, 144.4, 125.2, 52.2, 41.7, 27.9; MS $m/e$ (relative intensity) 283 ($(M + H)^+$, 65), 162 (65), 110 (100). Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.74; H, 6.52.

**2-Phenyl-1-vinylcyclopropanecarboxylic Acid (16) and 3-(2-Chloroethylidene)-2-oxo-5-phenyl-4,5-dihydrofuran (17).** A solution of cyclopropane **11** (0.37 g, 1.5 mmol) and $VOCl_2(OEt)$ (0.37 g, 7.5 mmol) in 10 mL of $CH_2Cl_2$ was refluxed for 30 h. Water was then added, and the mixture was extracted with $CH_2Cl_2$. The organic layer was washed with water and saturated NaCl solution, dried ($Na_2SO_4$), and concentrated. The residue was purified by chromatography on silica gel with ethyl acetate–hexane (3:7–4:6) as solvent gradient. **16**: yield 0.15 g (24%); mp 84–86 °C; IR (neat) 3500–2550, 1764, 1686, 1604 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 9.5 (br s, 1 H), 7.45–7.10 (m, 5 H), 5.82 (dd, $J$ = 17.3, 10.2 Hz, 1 H), 5.05 (d, $J$ = 10.2 Hz, 1 H), 4.97 (d, $J$ = 17.3 Hz, 1 H), 3.08 (dd, $J$ = 8.9, 7.5 Hz, 1 H), 1.97 (dd, $J$ = 8.9, 5.3 Hz, 1 H), 1.79 (dd, $J$ = 7.5, 5.3 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 180.0, 135.0, 130.8, 129.3, 127.9, 126.9, 117.9, 35.7, 33.3, 17.8. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.41; H, 6.44.

**17**: 0.10 g (15%); IR ($CCl_4$) 1755, 1575 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.50–7.28 (m, 5 H), 6.88 (tt, $J$ = 7.6, 2.9 Hz, 1 H), 5.58 (dd, $J$ = 8.1, 6.3 Hz, 1 H), 4.14 (d, $J$ = 7.6 Hz, 2 H), 3.47 (br dd, $J$ = 17.5, 8.1 Hz, 1 H), 2.90 (br d, $J$ = 17.5 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 169.7, 139.6, 133.4, 130.1, 128.9, 128.7, 125.3, 78.3, 39.7, 33.8; HRMS $m/e$ calcd for $C_{12}H_{11}O_2Cl$: 222.0448, found 222.0444. Heating of **16** with $VOCl_2(OEt)$ in dichloroethane under reflux for 12 h resulted in the formation of **17** in 59% yield.

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# Conjugated Macrocycles Related to the Porphyrins. 4.[1] Synthesis of a 23,24-Dioxa-5-oxophlorin[2]

Timothy D. Lash

*Department of Chemistry, Illinois State University, Normal, Illinois 61761-6901*

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Oxophlorins **1** are the keto tautomers of *meso*-hydroxyporphyrins **2**. Although the *meso*-hydroxyporphyrin structure can be trapped as, for example, the corresponding acetate by reaction with acetic anhydride–pyridine, the cross-conjugated oxophlorin system is favored in neutral solutions.[3] Oxophlorins **1** are important intermediates in the total synthesis of porphyrins,[4] and an iron complex of the hydroxy tautomer **2** is believed to be an intermediate in heme catabolism.[5] Monoprotonation of the oxophlorin system leads to monocations that also favor the keto form, but the hydroxyporphyrin tautomer is favored by the dications and metal complexes of these compounds.[3-6] Oxophlorins are relatively unstable in

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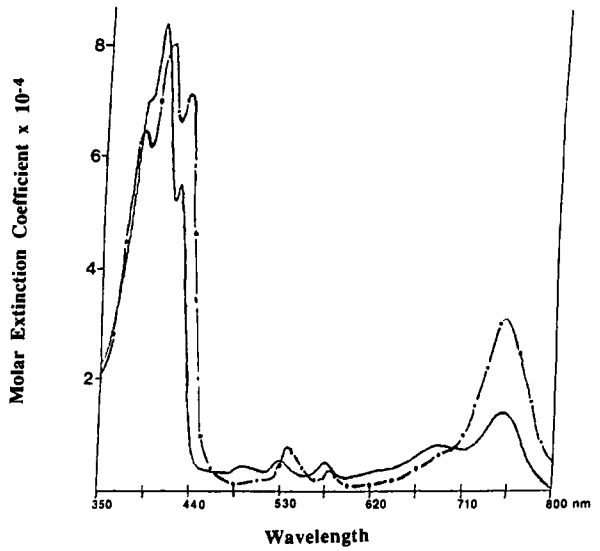
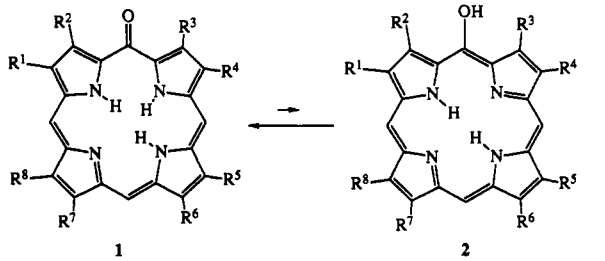
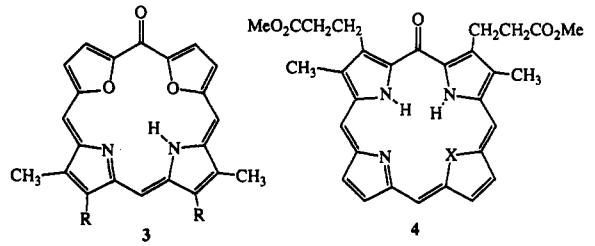



**Figure 1.** Electronic spectra of 23,24-dioxa-5-oxophlorin **5** in chloroform (—) and in 0.05% trifluoroacetic acid-chloroform (-·-·-).

solution and readily air oxidize to the corresponding radical species.[7]



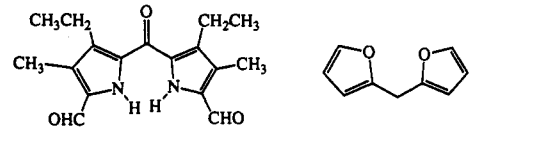
1 2



3 4

a. R = $CH_2CH_3$; b. R = $CH_2CH_2CO_2Me$ c. R = $CH_2CH_2CO_2Et$

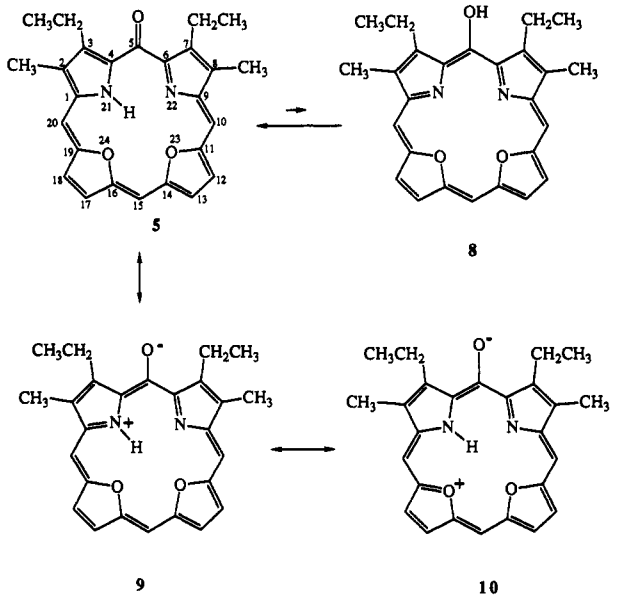
a. X = O; b. X = S



6 7

Although many examples of porphyrin analogs have been reported,[8] little work has been carried out on conjugated macrocycles related to the *meso*-hydroxyporphyrins/oxophlorins. We have previously reported[9-11] the synthesis of 21,22-dioxa-5-oxophlorins **3a-c**. IR and UV data suggested that these structures favored the keto form, and little, if any, of the corresponding hydroxyporphyrin analog was present in solution. The difuryl oxophlorin analogs **3a-c** also gave well-resolved proton and carbon-13 NMR spectra[10,11] that were consistent with the cross-conjugated structure **3**. In the presence of trace trifluoroacetic acid a monocationic species was formed which also favored the keto form. However, in 10% trifluoroacetic acid-chloroform, a dicationic species was observed whose NMR and UV spectra were in accord with the fully conjugated hydroxyporphyrin species. Furan and thiophene analogs, **4a** and **4b**, have also been described,[12] and these compounds have also been shown to favor the keto tautomers.

In order to extend these studies, we have investigated the acid-catalyzed condensation of 2,2′-difurylmethane (**7**) with a diformyl dipyrryl ketone **6** to give the 23,24-dioxa-5-oxophlorin **5**. Condensation of 2,2′-difurylmethane **7**[13] and dipyrrylketone **6**[14] in trifluoroacetic acid-chloroform, followed by extraction and chromatography on neutral alumina, gave a green band which crystallized from dichloromethane-ethanol as lustrous purple needles. Unfortunately, the yields were very low (2-3%), and this was attributed to the low reactivity of the furan nucleus towards electrophilic substitution. However, the yields were increased to 17% when the reaction was carried out in hydrobromic acid-acetic acid. The NMR, IR and UV spectra of the difuryl macrocycle supported the keto structure **5** and little, if any, of the enol tautomer **8** ap-



5 8

9 10

peared to be present in neutral solutions. The IR spectrum showed a prominent absorption at 1550 $cm^{-1}$, which would be expected for the cross-conjugated carbonyl moiety. In the aromatic region of the proton NMR spectrum, the furyl and meso protons appeared between 7.8 and 8.5 ppm, and these data are consistent with the absence of a porphyrin-like ring current. The carbon-13 NMR spectrum showed a resonance at 174.45 ppm, and this was consistent with the presence of the bridging carbonyl unit of structure **5**. The electronic spectrum of **5** in chloroform (Figure 1) was complex and showed three absorptions of moderate intensity in the Soret region. In conjunction, all of these

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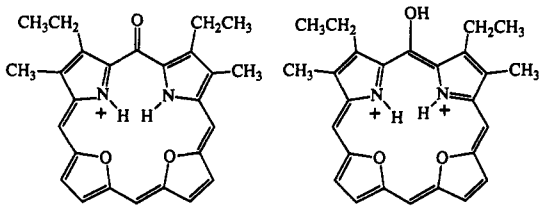
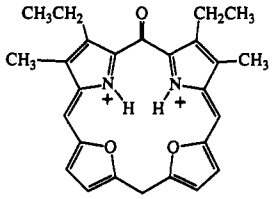
spectroscopic data suggested that the keto tautomer **5** was favored in solution, although dipolar resonance contributors such as **9** and **10** appear to make a considerable contribution. In the presence of 0.02% trifluoroacetic acid, a monocationic species **11** appeared to be formed, as evi-



**11**



**12**



**13**

denced by changes in the UV–vis spectrum (Figure 1). The absorptions near 400 nm were also of relatively low intensity, and this indicated that the monocation also existed primarily in the keto form. It is noteworthy that both **5** and **11** showed significant absorptions near 750 nm. Porphyrin analogs with absorption bands beyond 700 nm are presently under intense scrutiny as potential second generation photosensitizers in photodynamic tumor therapy,[15] and it is possible that the 23,24-dioxa-5-oxophlorin system **5** could be of value in this regard.

In 10% trifluoroacetic acid, an inky blue fully aromatic dication **12** was formed which exhibited a single intense Soret band at $\lambda_{max}$ 402 nm ($\log_{10} \epsilon = 5.28$). The proton and carbon-13 NMR spectra of **5** in 10% TFA-*d*-deuteriochloroform also supported the existence of the fully aromatic porphyrin-like dication. No proton exchange, apart from the NH's, was observed even after one month at room temperature and this indicated that C-protonated dications such as **13** are not in equilibrium with **12**. In this respect, **5** differs from macrocycle **3** which gives selective deuterium exchange under these conditions.[11] The monocations of true oxophlorins **1** are also susceptible to deuterium exchange at one of the methine bridging units.[3a]

In many ways the new oxophlorin system **5** is similar to the tetrapyrrolic oxophlorins **1** and the 21,22-dioxa-5-oxophlorins **3**. However, macrocycles **3** and **5** differ from **1** in that they give well-resolved NMR spectra and do not air oxidize to radical species. Unlike **1**, the difuryl macrocycles **3** and **5** do not react with acetic anhydride–pyridine to give acetoxyporphyrin analogs. The UV–vis spectra for each system differ considerably from one another. True oxophlorins **1** give royal blue solutions which exhibit blue fluorescence under long-wave ultraviolet light. Macrocycles **3** also gave blue solutions but produced an intense red fluorescence under longwave ultraviolet light. The new difuryl oxophlorin **5** gave green solutions and did not demonstrate any fluorescence. On the other hand, all three systems afforded a deep red fluorescence in 10% trifluoroacetic acid–chloroform solutions.

## Experimental Section

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer, and UV spectra were obtained on a Beckmann DU-40 spectrophotometer. NMR spectra were recorded on a Varian Gemini-300 NMR spectrometer. Mass spectral determinations were made at the Midwest Center for Mass Spectrometry at the University of Nebraska–Lincoln with partial support by the National Science Foundation, Biology Division (Grant No. DIR9017262). Elemental analyses were obtained from Micro-Analysis, Inc., Wilmington, DE 19808.

**3,3'-Diethyl-4,4'-dimethyl-2,2'-dipyrrylmethanone-5,5'-dicarboxaldehyde (6).** Prepared by the procedure of Clezy et al.:[14] mp 205–207 °C, softening at 198 °C (lit.[14] mp 200–202 °C); IR (Nujol mull) $\nu$ 3230 (NH str.), 1657, 1634 (C=O str.) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.22 (6 H, t, $J$ = 7.5 Hz, 2 × $CH_2CH_3$), 2.38 (6 H, s 2 × pyrrole-$CH_3$), 2.78 (4 H, q, $J$ = 7.5 Hz, 2 × $CH_2CH_3$), 9.28 (2 H, s, 2 × CHO), 11.1 (2 H, br, 2 × NH); $^{13}C$ NMR ($CDCl_3$) $\delta$ 8.21 (2 × pyrrole-$CH_3$), 15.00 (2 × $CH_2CH_3$), 17.27 (2 × pyrrole-$CH_2$), 130.12, 133.64, 134.34, 178.09 (2 × CHO), 178.68 (bridge CO).

**2,2'-Difurylmethane (7).** Prepared by the procedure of Dinelli and Marini:[13] bp 95 °C (30 Torr) (lit.[13] bp 66 °C (5 Torr)); $^1H$ NMR ($CDCl_3$) $\delta$ 4.00 (2 H, s, bridge $CH_2$), 6.08 (2 H), 6.30 (2 H) (4 × $\beta$-H), 7.33 (2 H, 2 × $\alpha$-H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 27.39 (bridge $CH_2$), 106.42 (3,3'-CH), 110.36 (4,4'-CH), 141.56 (5,5'-CH), 151.54 (2,2'-C).

**3,7-Diethyl-2,8-dimethyl-23,24-dioxa-5-oxophlorin (5).** A solution of 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrrylmethanone-5,5'-dicarboxaldehyde (**6**) (100 mg) and 2,2'-difurylmethane (**7**) (60mg) in 20 mL of acetic acid were added dropwise over 30 min to a stirred solution of acetic acid containing 10 drops of 30% HBr–acetic acid. The mixture was stirred for a further 3 h at room temperature, diluted with chloroform, and washed with water, 5% aqueous sodium bicarbonate solution, and water. The solvent was evaporated under reduced pressure and the dark residue chromatographed on Grade 3 alumina, eluting with dichloromethane. A major green fraction was collected and crystallization from dichloromethane–ethanol gave the oxophlorin analog as long gleaming purple needles (23 mg; 17%): mp > 300 °C; IR (KBr) $\nu$ 1550 $cm^{-1}$ (C=O str.); UV ($CHCl_3$): $\lambda_{max}$ ($\log_{10}$ $\epsilon$) 389 (4.84), 401 (4.92), 423 (4.74), 493 (3.64), 529 (3.74), 575 (3.69), 686 (3.91), 749 (414); UV (0.05% TFA–$CHCl_3$) $\lambda_{max}$ ($\log_{10}\epsilon$) 384 (4.81), 407 (4.90), 428 (4.85), 538 (3.90), 581 (3.58), 686 (infl.) (3.80), 751 (4.48); UV (10% TFA-$CHCl_3$) $\lambda_{max}$ ($\log_{10}\epsilon$) 402 (5.28), 5.36 (3.94), 578 (3.87), 620 (3.87), 706 (3.97); $^1H$ NMR ($CDCl_3$) $\delta$ 1.48 (6 H, t, $J$ = 7.4 Hz, 2 × $CH_2CH_3$), 2.85 (6 H, s, 2 × pyrrole-$CH_3$), 3.52 (4 H, q, $J$ = 7.4 Hz, 2 × $CH_2CH_3$), 4.15 (1 H, br, NH), 7.84 (1 H, s, 15-H), 8.06 (2 H, d, $J$ = 4.6 Hz, 13,17-H), 8.36 (2 H, s, 10,20-H), 8.39 (2 H, d, $J$ = 4.6 Hz, 12,18-H); $^1H$ NMR (10% TFA-*d*-$CDCl_3$) $\delta$ 1.66 (6 H, t, $J$ = 7.4 Hz, 2 × $CH_2CH_3$), 3.62 (6 H, s, 2 × pyrrole-$CH_3$), 4.19 (4 H, q, $J$ = 7.4 Hz, 2 × $CH_2CH_3$), 10.27 (2 H, d, $J$ = 4.8 Hz), 10.45 (2 H, d, $J$ = 4.8 Hz) (4 × furyl-H), 10.80 (1 H, s, 15-H), 10.90 (2 H, s, 10,20-H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 10.23, 14.51 (4 × $CH_3$), 20.54 (2 × $CH_2$), 89.30 (15-C), 103.98 (10,20-C), 121.23, 129.05, 134.78, 136.75, 141.37, 150.43, 150.59, 155.59, 174.45 (C=O); $^{13}C$ NMR (10% TFA-*d*-$CDCl_3$) $\delta$ 10.37, 13.76, 20.45, 96.04, 102.81, 132.57, 136.35, 137.19, 138.42, 138.77, 146.06, 154.21, 157.02; FAB MS $m/e$ 413 ($[M + H]^+$); HR FAB MS calcd for $C_{26}H_{24}N_2O_3$ + H 413.1865, found 413.1869. Anal. Calcd for $C_{26}H_{24}N_2O_3$: C, 75.7; H, 5.9; N, 6.8. Found: C, 75.3; H, 5.8; N, 6.6.

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**Supplementary Material Available:** Further spectroscopic data for 23,24-dioxa-5-oxophlorin 5 (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

# Rearrangements of 2,2′-Bis(methylene)dicyclopropyl

Kristi J. Snellings and Edward S. Lewis*

*Department of Chemistry, Rice University, P.O. Box 1892, Houston, Texas 77251*

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## Introduction

The substance 2,2′-bis(methylene)dicyclopropyl, 1, became available a few years ago. It was of interest to see if there were any new thermal reactions of this substance attributable to simultaneous reaction of both rings; the methylenecyclopropane rearrangement[1] of either half of the molecule was expected.

## Results

A new synthesis of 1 as a separable diastereomeric mixture is described, as are the rates and equilibrium of the interconversion of the two diastereomers and the identification of all detected monomeric products of thermal reaction in solution in mesitylene. A brief study in the gas phase at higher temperatures is also reported.

The measured initial rate constants and equilibrium constants of the *meso*- to *dl*-conversion are given in Table I. Equilibrium constants were calculated as the ratio of the forward to reverse rate constants. At higher temperatures in solution and in the gas phase we used the equation $K = [dl\text{-}1]/[meso\text{-}1]$ since kinetic data were unavailable and substantial reaction had taken place. This calculation assumes that the stereoisomer interconversion is fast compared to all irreversible reactions. The discrepancy between the solution- and gas-phase results can be attributed either to the different conditions or to a failure of the above assumption. There was no significant variation of the equilibrium constants with temperature either in solution or in the gas phase.

The rate data in Table I are described by the expressions (1) and (2). The activation energies (in kcal/mol) are slightly smaller than some literature values for related compounds,[2] and the preexponential values are also somewhat higher. The analytical problems at less than

$$k_f = 10^{14.1} \exp(-36.7 \pm 0.7/RT) \quad (1)$$

$$k_r = 10^{15.1} \exp(-38.5 \pm 0.2/RT) \quad (2)$$

5% reaction with (even at this low conversion) perceptible amounts of other products leads us to mistrust the precision given; the two expressions may not differ significantly.

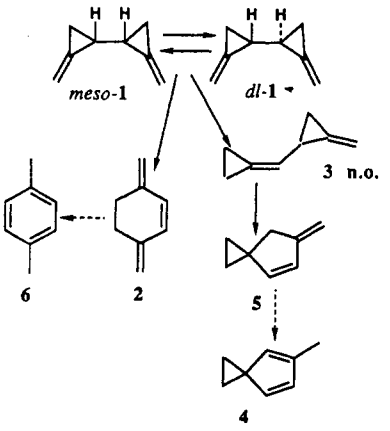
Scheme I shows the observed products from either isomer of 1, as well as one plausible intermediate, 3, the methylenecyclopropane rearrangement product which should rearrange rapidly to 5, in conformity with earlier results on vinylmethylenecyclopropanes.[3]

Table I. Rates[a] for the Conversion of the *meso*-1 to *dl*-1, $k_f$, the Reverse, $k_r$, and the Equilibrium Constant, $K$, in Mesitylene

| $t$, °C | $k_f$ s$^{-1}$ × 10$^6$ | $k_r$ s$^{-1}$ × 10$^6$ | $K$ |
|---|---|---|---|
| 131.1 | 1.61 ± 0.03 | 1.81 ± 0.06 | 0.89 ± 0.03[b] |
| 141.1 | 4.77 ± 0.10 | 5.5 ± 0.10 | 0.86 ± 0.16[b] |
| 151.1 | 14.0 ± 0.17 | 17.5 ± 0.01 | 0.80 ± 0.02[b] |
| 195[c] | | | 0.85 ± 0.07[c] |
| 292–352[c] | | | 1.12 ● 0.09[c,d] |

[a] Rate constants are the average of three to four individual measurements. [b] The equilibrium constant was calculated as ratio of the two rate constants given. [c] The equilibrium constant was calculated from the average ratio of *dl*-1 to *meso*-1 at the temperatures indicated; no kinetic data were collected at these temperatures. [d] These are gas-phase flash vacuum pyrolysis results; no systematic variation with temperature was noted.

**Scheme I**[a]




[a] And several dimers. Dashed arrows are secondary reactions. n.o. = not observed.

All other reactions were slower than the stereoisomer interconversion; no kinetic data on these were obtained. The structures shown in Scheme I were determined by NMR on samples separated by preparative GC methods. The major initial product was 2, which is itself thermally unstable. The other initial product is 5. Compounds 4, and 6, were shown to be artifacts derived from surface reactions and the GC separation artifacts of 5 and 2 respectively. Only 6 is stable for very long periods of heating.

The apparent 1,3 hydrogen shifts to give 4 and 6 suggested a possible free-radical chain with abstraction and readdition of allylic hydrogen. However, in mesitylene-$d_{12}$, no deuterium was incorporated from the solvent into either compound as shown by GCMS, so this radical chain does not occur in mesitylene solution.

The conversion to identified products was not quantitative; at least six dimers identified only as $C_{16}H_{20}$ by GC-mass spectra were found as well as higher molecular weight products. Yields were therefore not well determinable. However, at small extents of conversion the major product from 1 is 2, and in the gas phase the yield of 2 is always greater than that of 5 (counting 6 as part of 2 and 4 as part of 5) and is possibly as high as 70%. The fall in the product ratio with extent of conversion is presumably due to the low thermal stability of 2. Clearly, both

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(2) Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 2720.
(3) Billups, W. E.; Leavell, K. H.; Lewis, E. S.; Vanderpool, S. *J. Am. Chem. Soc.* **1973**, *95*, 8096.
(4) A reviewer suggests that the Cope product of 1, 1,2-dicyclopropenylethane, might be an intermediate in the *meso*- to *dl*-1. However, group additivity calculations show that this Cope product is less stable than 1 by about 51 kcal/mol. The observed activation energy for the *meso*- to *dl*-1 of 36–39 kcal/mol can hardly be this much in error, so this mechanism must be rejected.

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