la Provincia de Córdoba and Antorchas Foundation.

Registry No. 1, 591-50-4; 2, 24262-31-5; 3, 103-79-7; 4, 781-35-1; 5, 34438-71-6; 6, 451-40-1; 7, 1733-63-7; 8, 91120-35-3; 9, 14596-70-4; 10, 18137-96-7; 11, 6125-24-2; 14, 27252-54-6; 15, 70360-84-8; 16, 17272-66-1; 4-bromobenzophenone, 90-90-4; acetylacetone, 123-54-6; diethyl malonate, 105-53-3; anthrone, 90-44-8; nitromethane, 75-52-5; methyl *tert*-butyl ketone, 75-97-8; acetylphenone, 98-86-2; acetone, 67-64-1; 1-methylnaphthalene, 90-12-0; 4-methylbenzophenone, 134-84-9; phenyl radical, 2396-01-2.

Synthesis and Properties of 4,4,9,9-Tetramethyl[12]paracyclophane-5,6,7,8-tetrone†

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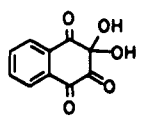
The synthesis of 4,4,9,9-tetramethyl[12]paracyclophane-5,6,7,8-tetrone (**26**) has been achieved in a multistep procedure. Compound **26** is the first cyclic tetraketone whose structure has been studied by X-ray analysis. The key intermediates were 4,4,9,9-tetramethyl[12]paracyclophane-6,7-dione (**22**), 6,7-bis[(trimethylsilyl)oxy]-4,4,9,9-tetramethyl[12]paracyclophane-5,7-diene (**24**), and two epimeric 5,8-dihydroxy-4,4,9,9-tetramethyl[12]-paracyclophane-6,7-diones **25a** and **25b**. X-ray analyses have been performed on **24**, **25b** and **26**. That on **24** reveals a dihedral angle of 57° between the two silylenol ether groups. The product analyses and the configurations of **25a** and **25b** together with the isolation of the bis(epoxide) intermediate **28** allow conclusions to be drawn on the oxidation mechanism of **24** with *m*-CPBA (Rubottom reaction). The stability of **26** is ascribed to steric factors.

Vicinal polyketones have been known for more than a century and have been well studied.[1] Although the first members of the acyclic series diphenyl triketone and diphenyl tetraketone were described nearly at the same time, in 1890[2] and 1892,[3] respectively, the properties of vicinal tetraketones were investigated much later[1,4] than those of vicinal triketones. The next higher homologue, diphenyl pentaketone,[5] was reported only recently. Data concerning cyclic polyketones are much more scarce. Before 1987, cyclic tetraketones were known only as hydrates such as **1** and **2**[6] or as strong electron-donor substitutents such as the salt of rhodizonic acid (**3**).[7]



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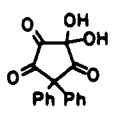

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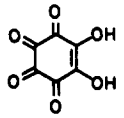
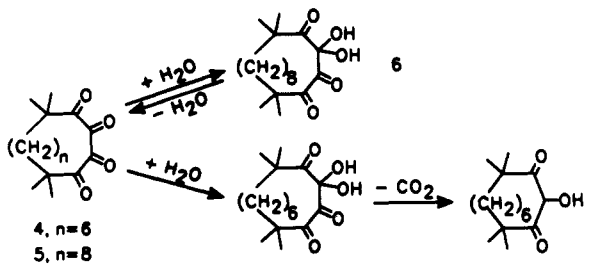


3

Our unsuccessful attempts to generate cyclic tetraketones from hydrates like **1**, **2** or related species[8] we ascribe to the fact that the accumulation of strong local dipoles (CO) together with the electron-withdrawing effect of phenyl groups leads to kinetically and thermodynamically unstable species. The partial cancellation of local dipoles can be attained by adding a strong electron-donor fragment to the vicinal polyketone as, for example, in the oxocarbons.[7] Another possible way to achieve stability is to increase the flexibility of the cyclic system. This idea led to the syntheses of **4** and **5**,[9] which were the first cyclic vicinal tetraketones isolated. It turned out that the hydrate of **5** is rather stable, whereas **4** reacts very rapidly with water accompanied by ring contraction[9] to an acireductone **8**.

Another way to stabilize such cyclic tetraketones is by transannular donor–acceptor interactions as indicated in **9**. The symbol X represents electron-rich atoms or groups



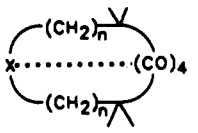
4, n=6
5, n=8

6

7

8

such as O, S, NR, or π-systems. In this paper, we wish to report our efforts to synthesize a vicinal tetraketone in the [12]cyclophane series. We chose this system because molecular modeling suggested that such a chain length should provide enough flexibility to arrange the $(CO)_4$ fragment in a helical geometry, as found for most acyclic and monocyclic compounds.



9

† Dedicated to Professor Mordecai B. Rubin on the occasion of his 65th birthday.

(1) Rubin, M. B. *Chem. Rev.* **1975**, *75*, 177. For most recent references see: Wassermann, H. H.; Cook, J. D.; Vu, C. B. *J. Org. Chem.* **1990**, *55*, 1701 and references cited therein. Liebeskind, L. S.; Wirtz, K. R. *J. Org. Chem.* **1990**, *55*, 5350 and references cited therein.
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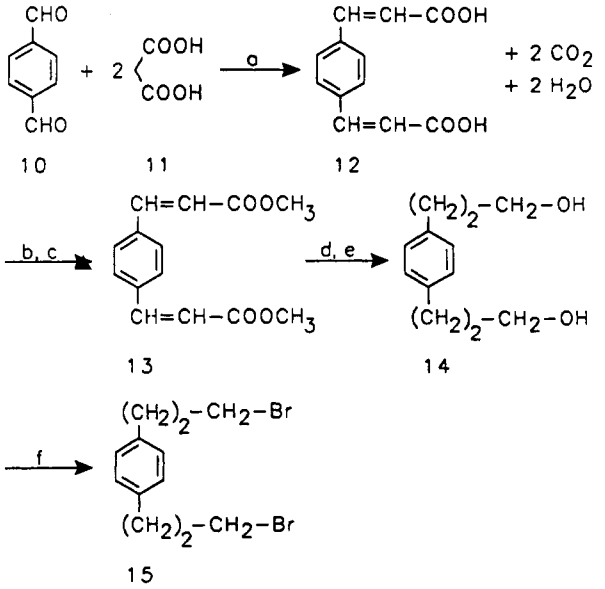
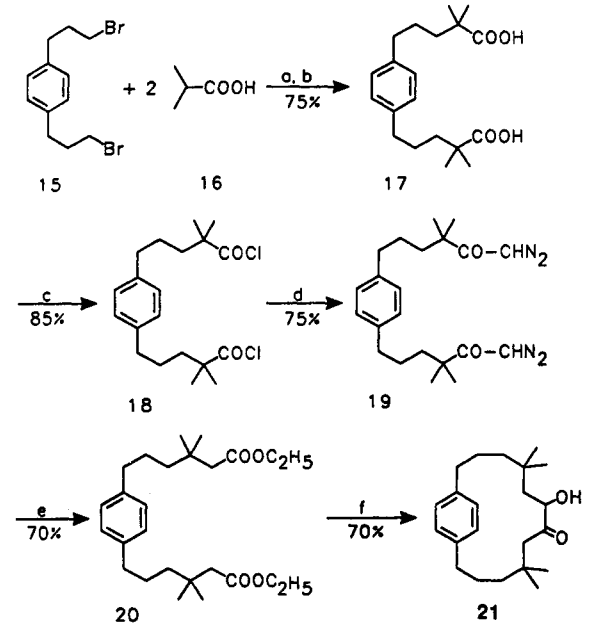
Scheme I[a]



[a] Key: (a) piperidine/pyridine, 110–130 °C; (b) $SOCl_2$/DMF; (c) CH_3OH, reflux; (d) H_2/Pd/C, THF, 40–50 °C; (e) $LiAlH_4$, THF, 50–60 °C; (f) HBr, 120–130 °C.

Scheme II[a]



[a] Key: (a) LDA; (b); H^+/H_2O; (c) PCl_5; (d) CH_2N_2; (e) *hν*, C_2H_5OH; (f) Na/xylene.

Synthesis

We started our investigations with the preparation of the known dibromide **15**.[10-13] The synthetic steps we used are shown briefly in Scheme I. The elongation of the alkyl chains is illustrated in Scheme II. The alkylation of the dianion of isobutyric acid (**16**) with **15** yields the diacid **17**.[14] The incorporation of the four methyl groups prevents the possible enolization at the ends of the $(CO)_4$ fragment in the target molecule. The homologization of **17** is achieved by the Arndt–Eistert reaction[15] via the acid chloride **18**. The bis(diazoketone) **19** rearranges to the diester **20** upon irradiation in ethanol. The acyloin ring closure[16] of **20** forms the cyclophane **21** in good yield.

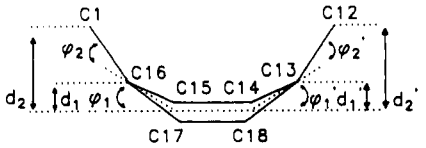


Figure 1. Definition of d and φ (see Table I) for the boatlike deformation of the phenyl ring in **24**, **25b**, and **26**.

Table I. Deviations of the Alkyl-Substituted Carbon Atoms of the Phenyl Ring (φ_1, φ_1') and the Benzylic Carbon Atoms (φ_2, φ_2') from the Planar Arrangement of 24, 25b, and 26 (See Figure 1)

	φ_1	φ_1'	φ_2	φ_2'
24	2.7	2.1	3.2	3.1
25b	2.3	2.2	2.7	5.1
26	3.1	3.8	4.5	5.1

Table II. Distances of the Alkyl-Substituted Carbon Atoms of the Phenyl Ring (d_1, d_1') and of the Benzylic Carbon Atoms (d_2, d_2') from the Plane Defined by C(14)–C(15)–C(17)–C(18)

	d_1 (Å)	d_1' (Å)	d_2 (Å)	d_2' (Å)
24	0.03	0.03	0.17	0.19
25b	0.03	0.03	0.15	0.22
26	0.04	0.05	0.27	0.25

The final steps are summarized in Scheme III. Oxidation of **21** to the diketone **22** is carried out with $Cu(OAc)_2 \cdot H_2O$.[17] The silylation to the bis(silylenol ether) **24** was accomplished in two separate steps; first, the mono(silylenol ether) **23** was prepared, and second, it was transformed to **24**. This was done because none of our efforts to generate **24** from **22** in a one-pot procedure worked, neither use of the bases lithium diisopropylamide (LDA)[18] or sodium bis(trimethylsilyl)amide[19,20] nor a direct silylation with trimethylsilyl triflate[21,22] gave acceptable yields. The reluctance of **22** to submit to a direct bis-silylation can be attributed to steric effects. However, the steric crowding worked to our advantage in that it rendered both **23** and **24** relatively stable toward hydrolysis. X-ray investigations carried out on single crystals of **24** (see below) confirmed the *Z,Z* configuration of the double bonds in **24**, which had been indicated by ^1H NMR. From the temperature dependence of the ^{13}C NMR signals of the aromatic ring (129.5 and 129.9 ppm, CH), we estimated an activation enthalpy[23] of 67 kJ/mol for the rotation of the aromatic ring in **24** around the C(1)–C(16) and C(12)–C(13) axis. The oxidation of **24** with *m*-chloroperbenzoic acid (*m*-CPBA, Rubottom reaction[24-27]) afforded

(10) Dutt, S. *Quart. J. Ind. Chem. Soc.* **1925**, *1*, 297.
(11) Ruzicka, L.; Buijs, J. B.; Stoll, M. *Helv. Chim. Acta* **1932**, *15*, 1220.
(12) Matsuoka, T.; Negi, T.; Otsubo, T.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1825.
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(17) Bloch, H.; Lehr, H.; Erlenmeyer, H.; Vogler, K. *Helv. Chim. Acta* **1945**, *28*, 1410.
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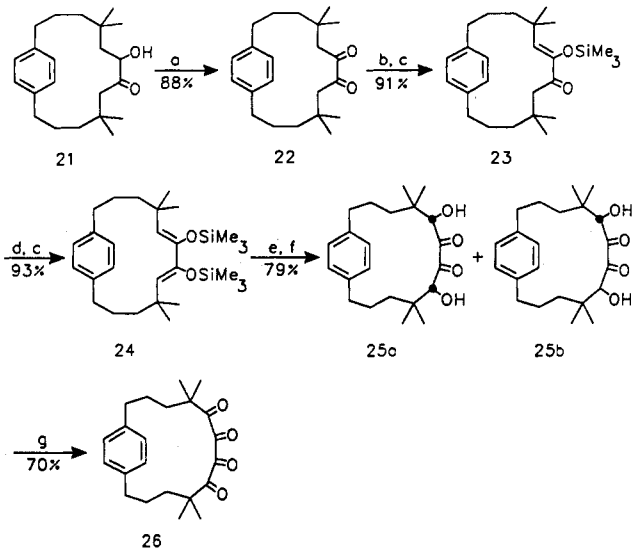
(23) Günther, H. *NMR-Spektroskopie*; Georg Thieme Verlag; Stuttgart, 1979.

Scheme III[a]



[a] Key: (a) $Cu(OAc)_2 \cdot H_2O$/HOAc; (b) $NaN(SiMe_3)_2$; (c) $ClSiMe_3$; (d) LDA; (e) *m*-CPBA/CH_2Cl_2; (f) CH_3OH; (g) $(COCl)_2$/DMSO, NEt_3.

two diastereoisomeric dihydroxy diketones **25a** and **25b** in the ratio of 3:1. An X-ray investigation on single crystals of **25b** exhibited either the *RR* or *SS* configuration and obviated the need of assigning the configuration (see below) through spectroscopy. The further oxidation of **25** to the cyclic vicinal tetraketone **26** was achieved by using DMSO/$(COCl)_2$ according to Swern;[28] whereas attempts to use *N*-bromosuccinimide (NBS) also caused bromination at the benzylic position. The new tetraketone proved to be very stable toward reactions with nucleophiles such as water.

X-ray Investigations and Discussion

As mentioned above, we were able to obtain single crystals of **24**, **25b**, and **26**. Common to all three molecules is a boatlike deformation of the aromatic ring caused by the bridge. The substituted atoms in the para positions of the phenyl ring lie out of the plane defined by the four unsubstituted carbon atoms of the phenyl ring (see Figure 1). The angles φ_1 and φ_1', which describe the boatlike deformation of the phenyl ring, and the angles φ_2 and φ_2', which describe the deviations of the bond vectors C(aromatic)–C(benzylic) from the bow and stern planes of the boatlike phenyl ring are collected in Table I. In Table II we list the distances d_1 and d_2. The deformations of the phenyl ring found are similar to those reported for [3.3]paracyclophane[29] or [3]paracyclotropoquinophane.[30] The strongest deformation of the aromatic ring is found for the tetraketone **26**.

In the case of the diene **24** (see Figure 2) we were interested in the torsional angle τ between the two silylenol ether moieties and the configuration of the double bonds. The considerable deviation from coplanarity (τ = 56.9 (5)°)

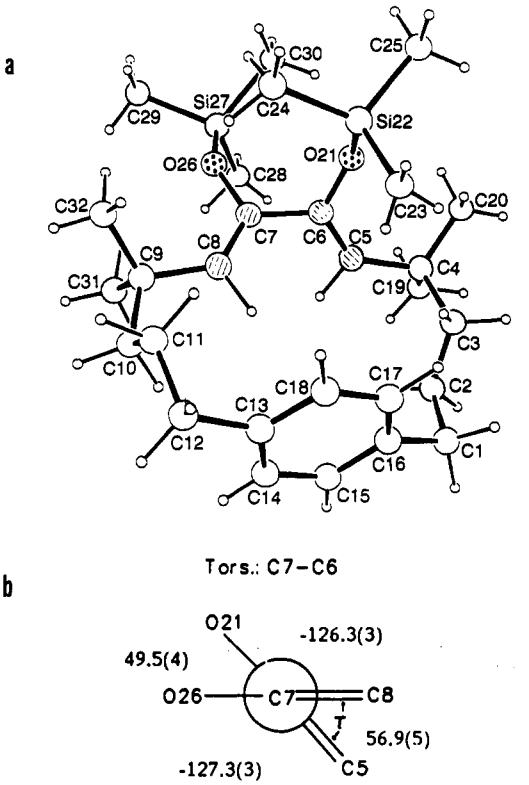


Figure 2. (a) Molecular structure of **24**. The stippled circles represent oxygen atoms, the striped circles represent diene carbons. (b) Newman projection along C(7)–C(6) to show the dihedral angle τ between the olefinic moieties.

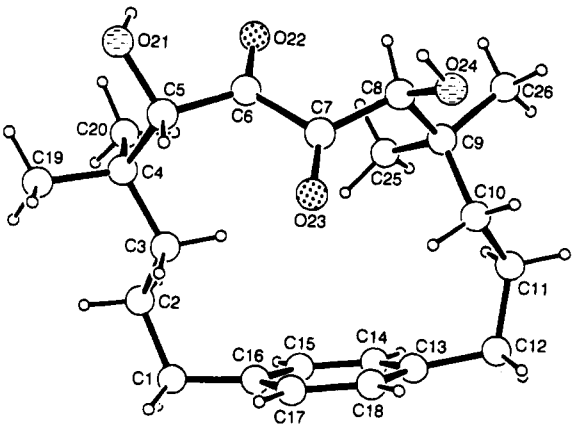


Figure 3. Molecular structure of **25b**. The stippled circles represent oxygen atoms, the dashed circles oxygen atoms of the OH groups.

of the butadiene unit can be attributed to the bulkiness of the (trimethylsilyl)oxy substitutents. The structure of **25b** (see Figure 3) is not only important for the assignment of the configurations of the two diastereoisomers **25a** and **25b**, but also for the mechanism of the oxidation reaction of **24** to **25a** and **25b** with *m*-CPBA. For the Rubottom reaction it is generally assumed that the first step is the formation of the corresponding epoxide followed by rearrangement to the α-siloxy ketone. Several groups have isolated and identified such intermediates.[31-33] In our case, where a double Rubottom reaction takes place, we have isolated the bis(epoxide) **28**. Its configuration is known

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(25) Brook, A. G.; Macrae, D. M. *J. Organomet. Chem.* **1974**, *77*, C19.
(26) Hassner, A.; Reuss, R. H.; Pinnick, H. W. *J. Org. Chem.* **1975**, *40*, 3427.
(27) Rubottom, G. M.; Gruber, J. M.; Boeckman, R. K., Jr.; Ramaiah, M.; Medwid, J. B. *Tetrahedron Lett.* **1978**, 4603.
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(32) Mori, K.; Sakakibara, M.; Okada, K. *Tetrahedron* **1984**, *40*, 1767.
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Scheme IV

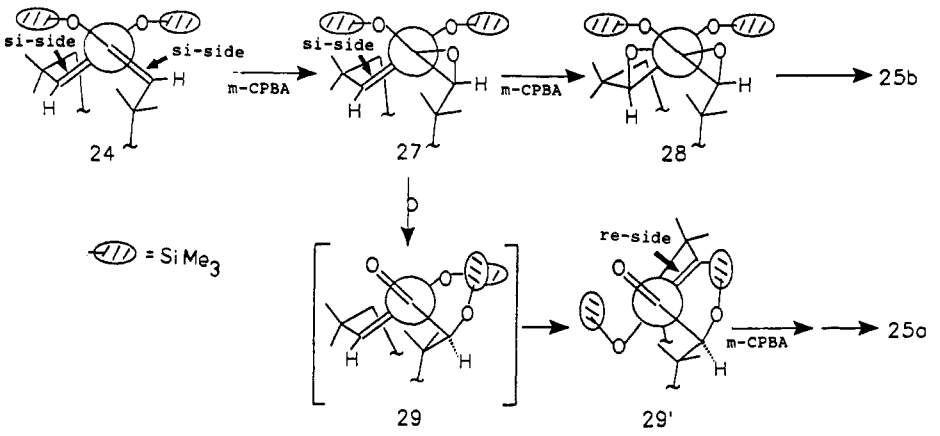
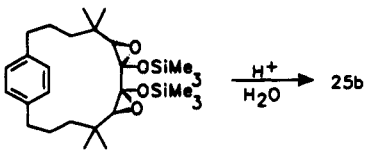


Table III. Selected Geometrical Parameters of 26, 30, and 31. The Numbering Refers to That Shown for 26 in Figure 4. The esd's of the Bond Distances of 30 are 0.002–0.003 Å[34]

bond distances (Å)			
bonds	26	30	31
O(21)–C(5)	1.203 (5)	1.218	1.221 (3)
O(22)–C(6)	1.208 (5)	1.196	1.194 (3)
O(23)–C(7)	1.201 (5)	1.196	1.200 (4)
O(24)–C(8)	1.206 (5)	1.218	1.220 (3)
C(4)–C(5)	1.522 (6)	1.463	1.465 (3)
C(5)–C(6)	1.541 (6)	1.541	1.522 (4)
C(6)–C(7)	1.541 (6)	1.523	1.552 (4)
C(7)–C(8)	1.543 (6)	1.541	1.512 (4)
C(8)–C(9)	1.527 (6)	1.463	1.465 (3)
torsional angles			
angles	26	30	31
O(21)–C(5)–C(6)–O(22)	−141.2 (4)	144.1	144.6
O(22)–C(6)–C(7)–O(23)	−132.7 (4)	128.5	−24.2
O(23)–C(7)–C(8)–O(24)	−145.4 (4)	144.1	128.4

through the NMR monitored hydrolysis that produces the dihydroxydiketone **25b** (*RR* or *SS*).



28

The isolation of **25a** and **25b** (see Schemes III and IV) in varying ratios depending on different reaction conditions (7:3 in methylene chloride) suggests two possible reaction paths: first a *si* side attack (a *re* side attack is equally possible) of the *m*-CPBA molecule occurs on **24** to yield the monoepoxide **27**. This compound is either transformed by another *si* (*re*) side attack to the bis(epoxide) **28** or it rearranges to the α-siloxy ketone **29** (see Scheme IV). Hydrolysis of **28** yields **25b** (*RR* or *SS*). The steric interactions between the bulky $OSiMe_3$ groups in the rearranged α-siloxy ketone **29** can be diminished by a simple rotation around the central C–C bond. This leads to conformation **29′**, in which the bulky groups are far apart. In **29′** the *re* (*si*) side attack of the oxidant is favored, and thus **25a** (RS) finally results. The sterically hindered attack of the second *m*-CPBA molecule should lead mainly to the isomer **25a** via the rearranged species **29′**, as we have indeed observed. Ongoing studies with other bis(silyloxy)dienes should help us to further clarify the two proposed reaction paths.

In Figure 4 diagrams of the molecular structure of **26** are shown as determined by X-ray analysis. In Table III

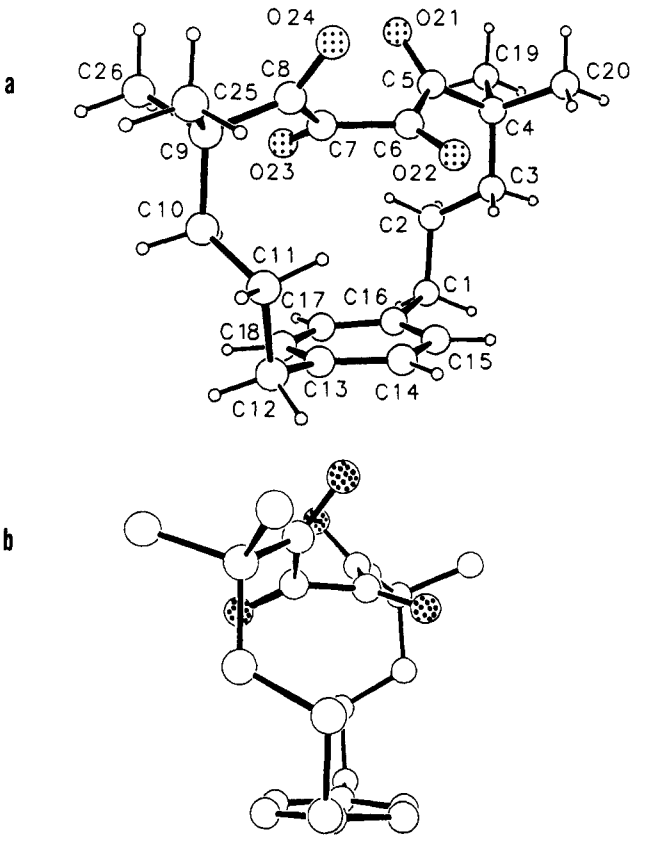
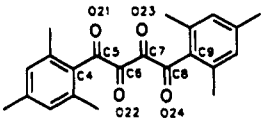
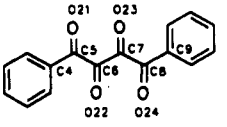


Figure 4. (a) Molecular structure of **26**. (b) Side view approximately along the C(1)–C(12) axis. The stippled circles represent carbonyl oxygens.

we have compared some of the geometrical parameters found for **26** with those reported for 1,5-dimesityl tetraketone (**30**)[34] and 1,5-diphenyltetraketone (**31**).[35]



30



31

It can be seen that the four carbonyl groups of **26** are arranged in a helix with the torsional angles −141.2°, −132.7°, and −145.4° (see Table III). Similar torsional

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angles are reported for **30** (144.1°, 128.5°, 144.1°),[34] while for **31** the central torsional angle is −24.2°. The helical arrangement of the CO groups in **26** is due to repulsive interactions between the oxygen atoms. Short O···O contacts (O(21)···O(23) 3.063 (4) Å; O(22)···O(24) 3.016 (4) Å) between nonadjacent CO groups prevent an all-transoidal arrangement of the CO groups. It is interesting to note that force field calculations which consider only dipole–dipole interactions of the CO groups predict[36] a broad minimum into which this helical arrangement fits. This arrangement seems to be preferred despite the strain of this system which shows up in the deformation of the phenyl ring.

From the data in Table III we notice that the central CO–CO bond length (C(6)–C(7)) varies with the torsional angle. In the case of **31** where the torsional angle O-(22)–C(6)–C(7)–O(23) is small (−24.2°), the C(6)–C(7) distance equals 1.552 Å. In **30** where the torsional angle is large, the C(6)–C(7) distance is found to be 1.523 Å. For **26**, whose torsional angle is similar to **30**, we therefore expect a similar C(6)–C(7) distance. The lengthening (1.541 Å) is due to the additional strain of the [12]-cyclophane moiety. In comparison with its other cyclic and acyclic congeners the tetraketone **26** is notably reluctant to react with nucleophiles such as H_2O. We attribute this to steric effects. The side view of the molecular structure (see Figure 4) shows that an attack from the side of the aromatic ring is prevented by the bridge and the geminal methyl groups. In addition an attack from the side of the $(CO)_4$ moiety is hindered by the fence of negatively charged oxygen atoms.

Conclusions

We have presented the synthesis of an especially stable cyclic vicinal tetraketone. The X-ray investigation reveals a sterically protected $(CO)_4$ moiety with a helical arrangement of the CO groups. On the synthetic path from the bis(silylenol ether) **24** to the tetraketone **26** we could isolate the bis(epoxide) **28** and the dihydroxy diketones **25a** and **25b**. These products suggest two paths for the oxidation of **24**: either the bis(epoxide) is formed which leads to **25b** or the monoepoxide rearranges to the siloxy ketone **29** before the second epoxidation takes place in which case **25a** is the final product.

Experimental Section

General. All melting points are uncorrected. The NMR spectra are measured with a Bruker AS 200 (^{1}H NMR at 200 MHz and ^{13}C at 50.23 MHz), Varian EM 390 and EM 360 (^{1}H NMR at 90 and 60 MHz, respectively) in $CDCl_3$ using either the solvent (200 MHz) or Me_4Si as internal standard (δ; J(Hz)). The mass spectra refer to data from a Vakuum Generators ZAB instrument (EI, 100eV), IR spectra were recorded with Perkin-Elmer 580B and Beckmann 4200 instruments. UV light absorption data were recorded in CH_2Cl_2 by using a Varian Cary 17D spectrometer.

X-ray Analysis. For the structure analyses, crystals of **24** (colorless prisms) from pentane, **25b** (orange needles) from ether and, **26** (red prisms) from methylene chloride were used. The crystallographic data are listed in Table IV. The data were collected on an automatic diffractometer (CAD4, Enraf-Nonius, Mo-K_α radiation, graphite monochromator, $\omega - 2\theta$ scan), and Lorentz and polarization corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F with anisotropic thermal parameters for the carbon, oxygen, and silicon atoms. The positions of the hydrogen atoms were calculated according to stereochemical requirements and were refined isotropically. Anomalous dispersion was taken into account for carbon, oxygen, and silicon atoms. The atomic coordinates are given as supplementary material. The SDP program system[37] was used on a MICRO-VAX 3100 computer.

Table IV. Crystallographic Data and Refinement Parameters of 24, 25b, and 26

	24	25b	26
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$C2/c$	$P2_12_12_1$
Z	4	8	4
a, Å	9.919 (2)	35.580 (6)	8.223 (2)
b, Å	17.258 (3)	5.971 (1)	15.600 (4)
c, Å	18.018 (3)	20.568 (2)	15.867 (3)
β, deg	100.04 (1)	111.23 (1)	90
crystal size, mm	0.5 × 0.5 × 0.35	0.5 × 0.35 × 0.2	0.35 × 0.35 × 0.5
max $(\sin\theta)/\lambda$	0.61	0.66	0.66
collected reflexions	7670	4938	2764
unique reflexions	5735	4865	2764
obsd reflexions ($I \geq 2.5\sigma(I)$)	2768	2787	1475
refinement R factors	0.053	0.040	0.053

1,4-Bis(4-carboxy-4-methylpentyl)benzene (17). To a cooled solution (−20 °C) of diisopropylamine (45.0 g, 0.45 mol) in absolute THF (450 mL) was added n-butyllithium (280 mL, 0.45 mol; 1.5 M in n-hexane) under argon. After the solution was stirred for 45 min, isobutyric acid (**16**) (17.6 g, 0.2 mol) was added dropwise at −20 °C. The mixture was then warmed to 50 °C and stirred for 2.5 h. The resulting clear light yellow solution was again cooled (−20 °C), and dibromide **15** (32 g, 0.1 mol) in absolute THF (100 mL) was added at a rate such that the temperature did not exceed 10 °C. The solution was stirred for 2 h at room temperature, whereupon a precipitate formed, and then an additional 1 h at 40 °C. The cooled (−5 °C) mixture was acidified with dilute HCl. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL), and then the combined organic phases were washed with water (2 × 100 mL) and dried (Na_2SO_4), and the solvent was evaporated. The remaining oil solidified slowly and yielded 31.6 g of **17** (75%). The raw material was recrystallized from THF/hexane as a colorless solid: mp 125–126 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.16 (s, 12 H), 1.56 (m, 8 H), 2.54 (m, 4 H), 7.07 (s, 4 H), 10.8 (s, H/D, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.9 (CH_3), 27.8 (CH_2), 36.6 (CH_2), 41.1 (CH_2), 42.5 (C), 129.3 (CH), 140.2 (CH), 182.6 (COOH). Anal. Calcd for $C_{20}H_{30}O_4$ (334.5): C, 71.82; H, 9.04. Found: C, 72.08; H, 9.20.

1,4-Bis[4-(chloroformyl)-4-methylpentyl]benzene (18). The bis(acid) **17** (20 g, 0.06 mol) was mixed with PCl_5 (26 g, 0.125 mol) at once. After a short period a vigorous reaction occurred; the resulting solution was stirred 6 h at room temperature. The $POCl_3$ was removed at 50 °C by vacuum distillation at 25 Torr and the residual PCl_5 by vacuum sublimation at 0.1 Torr. The resulting crude material was used directly in the next step or could be purified by distillation at 118–122 °C (0.1 Torr) to afford a pale yellow liquid that crystallized slowly: ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.2 (s, 12 H), 1.6 (m, 8 H), 2.6 (m, 4 H), 7.1 (s, 4 H).

1,4-Bis(6-diazo-4,4-dimethyl-5-oxohexyl)benzene (19). To a freshly prepared solution of diazomethane (~0.13 mol) in ether (350 mL) was added dropwise a solution of **18** (10.10 g, 27 mmol) in dry ether (150 mL) over a period of 5 h at 0 °C. After the solution was stirred for an additional 12 h, the volume of the solution was reduced to 150 mL at O °C. Cooling in a dry ice/methanol bath yielded yellow-green crystals of **19**, 7.8 g (75%). A sample was recrystallized from CCl_4: mp 71–72 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.1 (s, 12 H), 1.52 (m, 8 H), 2.52 (m, 4 H), 5.3 (s, 2 H), 7.05 (s, 4 H); IR ($CDCl_3$) 2958, 2920, 2098, 1622 cm^{-1}. Anal. Calcd for $C_{22}H_{30}N_4O_2$ (382.5): C, 69.08; H, 7.91; N, 14.65. Found: C, 68.55; H, 8.05; N, 14.22.

1,4-Bis[4,4-dimethyl-5-(ethoxycarbonyl)pentyl]benzene (20). A degassed solution containing bis(diazoketone) **19** (7.5 g, 20 mmol) in dry ethanol (450 mL) was irradiated in a 500-mL quartz photoreactor equipped with a Philips HPK 125W BA 15D lamp for ca. 12 h (monitored by TLC). Removal of the solvent left a brown oil which upon flash chromatography (silica gel, CH_2Cl_2) or vacuum distillation (bp 140–145 °C (0.02 Torr)) yielded

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5.75 g (70%) of a colorless liquid **20**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.00 (s, 12 H), 1.25 (t, J = 8.5 Hz, 6 H), 1.37 (m, 4 H), 1.60 (m, 4 H), 2.19 (s, 4 H), 2.57 (t, J = 9 Hz, 4 H), 4.09 (q, J = 8.5 Hz, 4 H), 7.10 (s, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.9 (CH_3), 26.8 (CH_2), 27.9 (CH_3), 33.8 (C), 36.8 (CH_2), 42.5 (CH_2), 46.5 (CH_2), 60.3 (CH_2), 128.8 (CH), 140.4 (C), 172.7 (COOR). Anal. Calcd for $C_{26}H_{42}O_4$ (418.6): C, 74.60; H, 10.11. Found: C, 74.65; H, 10.19.

7-Hydroxy-4,4,9,9-tetramethyl[12]paracyclophan-6-one (21). To a degassed suspension of sodium (2.53 g, 110 mmol) in dry refluxing xylene was added a solution of **20** (10.0 g, 24.2 mmol) in dry, degassed xylene (100 mL) under argon and constant stirring (Ultra-Turax, 4000–6000 rpm) over 24 h through the condenser. After being stirred for 1 additional h, the reaction mixture was cooled to −5 °C. Over the course of 45 min a mixture of glacial acetic acid and xylene (1:1, 150 mL) was added to the reaction mixture (which was still under argon) followed by water (100 mL). The water phase was extracted with xylene (2 × 30 mL). The combined organic phase was washed with water (3 × 100 mL), dried ($MgSO_4$), and concentrated to a yellow brown oil. The crude material was purified by flash chromatography (silica gel, CH_2Cl_2) followed by recrystallization from ether to yield 5.6 g (70%) of **21** as colorless crystals: mp 127–128 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.74 (dd, J_4 = 14.8 Hz, J_3 = 9.1 Hz, 1 H), 0.81 (s, 3 H), 0.85 (s, 3 H), 0.91 (s, 3 H), 0.94 (s, 3 H), 1.02–1.48 (m, 6 H), 1.48–1.80 (m, 4 H), 1.66 (d, J_5 = 16.5 Hz, 1 H), 2.27–2.50 (m, 2 H), 2.53 (d, J_1 = 7 Hz, 1 H), 2.51–2.78 (m, 2 H), 3.41–3.54 (ddd, J_1 = 7 Hz, J_2 = 2 Hz, J_3 = 9.1 Hz, 1 H), 7.00–7.12 (m, 4 H); IR (KBr) 3500, 2925, 2860, 1700 cm^{-1}. Anal. Calcd for $C_{22}H_{34}O_2$ (330.5): C, 79.95; H, 10.37. Found C, 79.82; H, 10.52.

4,4,9,9-Tetramethyl[12]paracyclophane-6,7-dione (22). A suspension containing acyloin **21** (3.0 g, 9 mmol), Cu(II) acetate·H_2O (3, 7 g, 18 mmol), and a mixture of glacial acetic acid and water (2:1, 120 mL) was heated to 120–140 °C to yield a solution. During heating for an additional 8 h the color of the solution changed from green to blue and Cu_2O precipitated. Ice water was added (100 mL), and the mixture was extracted with ether (4 × 50 mL). The organic phase was neutralized with a $NaHCO_3$ solution and solid $NaHCO_3$, dried ($MgSO_4$), and evaporated to afford a yellow solid. The crude material was subjected to flash chromatography (silica gel, CCl_4), which yielded 2.65 g (90%) of **22** as yellow crystals: mp 111.5–113 °C; ^{1}H NMR (50 MHz, $CDCl_3$) δ 0.90 (s, 12 H), 1.01–1.18 (m, 4 H), 1.36–1.56 (m, 4 H), 2.29 (s, 4 H), 2.45–2.61 (m, 4 H), 7.00 (s, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 28.6 (CH_2), 28.7 (CH_3), 33.8 (C), 35.4 (CH_2), 37.4 (CH_2), 44.2 (CH_2), 129.6 (CH), 140.2 (C), 199.7 (CO); IR ($CDCl_3$) 2926, 2856, 1707, 1698 cm^{-1}; UV (cyclohexane) (λ_{max} (nm), (log ϵ)) 259 (2.61), 262 (2.66), 273 (2.62), 450 (1.38). Anal. Calcd for $C_{22}H_{32}O_2$ (328.5): C, 80.44; H, 9.82. Found: C, 80.32; H, 9.98.

7-(Trimethylsiloxy)-4,4,9,9-tetramethyl[12]paracyclophan-7-en-6-one (23). To a solution of the diketone **22** (2.00 g, 6 mmol) in dry THF (40 mL) was added under argon a solution of sodium bis(trimethylsilyl)amide (1.21 g, 6.6 mmol) in dry THF (20 mL) at −40 °C. After being stirred for 2.5 h at −40 °C the reaction was quenched with trimethylchlorosilane (1.10 g, 10 mmol). After being warmed to room temperature the mixture was stirred for another 3 h, then the solvent (THF) was removed at 10 °C. The residue was taken up several times with n-pentane (3 × 70 mL), and the remaining precipitate filtered off through Celite. Evaporation of the solvent afforded crude material, which was further purified by flash chromatography (silica gel, CH_2Cl_2) to yield 2.24 g (93%) of **23** as white crystals: mp 107–108 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 0.85 (s, 6 H), 1.05 (s, 6 H), 1.13–1.28 (m, 2 H), 1.28–1.44 (m, 2 H), 1.44–1.60 (m, 4 H), 1.59 (s, 2 H), 2.45–2.60 (m, 4 H), 4.65 (s, 1 H), 7.14 (s, 4 H); ^{13}C NMR δ (50 MHz, $CDCl_3$) 2.4 (CH_3Si), 26.1 (CH_2), 26.2 (CH_3), 27.0 (CH_3), 28.9 (CH_2), 33.8 (C), 35.5 (CH_2), 35.6 (CH_2), 36.0 (C), 42.6 (CH_2), 42.7 (CH_2), 44.3 (CH_2), 129.8 (CH), 130.2 (CH), 131.6 (CH=C), 140.5 (C), 141.2 (C), 150.7 (COSi), 198.6 (CO); UV (CH_2Cl_2) (λ_{max} (nm), (log ϵ)) 258 (2.95), 315sh (1.95); HRMS (EI, 70 eV) calcd for $C_{28}H_{48}O_2Si_2$ 400.2798, found 400.2765, m/z (relative intensity) 400.2765 (M^+, 25), 385.2549 ($M^+ - CH_3$, 41), 372.2819 ($M^+ - CO$, 72), 73.0472 (100). Anal. Calcd for $C_{25}H_{40}O_2Si$ (400.7): C, 74.94; H, 10.06. Found: C, 75.11; H, 10.03.

6,7-Bis(trimethylsiloxy)-4,4,9,9-tetramethyl[12]paracyclophane-5,7-diene (24). To a freshly prepared solution of LDA from diisopropylamine (606 mg, 6 mmol, in 30 mL dry THF) and n-butyllithium (4 mL, 6 mmol, 1.5 M in n-hexane) was added dropwise a solution of monosilyl ether **23** (2.00 g, 5 mmol) in dry THF (30 mL) under argon at −40 °C. The solution was stirred for 1 h at −40 °C and then quenched with trimethylchlorosilane (1.36 g, 12.5 mmol). The cooling bath was removed and the stirring continued for another 2.5 h. The solvent was evaporated at 10 °C, the mixture was taken up in n-pentane, and the precipitate was filtered off. Again, the crude material was purified by flash chromatography (silica gel, cyclohexane, or n-pentane) to yield 2.20 g (93%) of **24** as white crystals: mp 112–113 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.08 (s, 8 H), 0.91 (s, 6 H), 1.01 (s, 6 H), 1.18–1.37 (m, 4 H), 1.37–1.60 (m, 4 H), 2.29–2.60 (m, 4 H), 3.62 (s, 2 H), 7.07 (s, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 1.4 (CH_3Si), 27.7 (CH_3), 28.5 (CH_3), 28.8 (CH_2), 35.5 (C), 35.7 (CH_2), 42.4 (CH_2), 118.4 (CH=C) 129.5 (CH), 129.9 (CH), 141.4 (C), 149 (COSi); HRMS (EI, 70 eV) calcd for $C_{28}H_{48}O_2Si_2$ 472.3193, found 472.3207, m/z (relative intensity) 472.3207 (M^+, 21), 457.2919 ($M^+ - CH_3$, 12), 444.2855 ($M^+ - CO$, 9), 73.0465 (100).

5,8-Dihydroxy-4,4,9,9-tetramethyl[12]paracyclophane-6,7-dione (25). Procedure A. A cooled and dried solution of metachloroperbenzoic acid (380 mg, 2.2 mmol) in CH_2Cl_2 (30 mL) was added dropwise to a solution of the bis(silylenol ether) **24** (500 mg, 1.05 mmol) in dry CH_2Cl_2 (10 mL) under argon at 0 °C. After being stirred for 60 min at 0 °C the solution was refluxed for 16 h, cooled, washed sequentially with $NaHSO_3$ (10 mL) and $NaHCO_3$ (5 × 15 mL) solutions, and dried ($MgSO_4$). After removal of the solvent, the orange residue was refluxed in aqueous methanol (50 mL) for 2 h. Concentration left a yellow to orange colored residue of **25**. Purification and separation were achieved by flash chromatography (silica gel, CH_2Cl_2) to yield 230 mg (61%) **25a** and 70 mg (18%) **25b** as orange to yellow crystals.

Procedure B. Same as procedure A, except dry ether was employed as solvent and the reaction mixture was stirred at room temperature for 35 h. The workup followed either procedure A or was accomplished by flash chromatography (silica gel, CH_2Cl_2) to afford 190 mg (50%) **25a** and 80 mg (21%) **25b** as orange to yellow crystals. Analytical properties are as follows. **5(*R**),8(*S**)-Dihydroxy-4,4,9,9-tetramethyl[12]paracyclophane-6,7-dione (25a)**; mp 126–127 °C; R_f 0.15 (silica gel, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.78 (s, 6 H), 0.88 (s, 6 H), 0.71–0.98 (m, 2 H), 0.98–1.22 (m, 2 H), 1.46–1.72 (m, 4 H), 2.32 (d, H/D, J = 8.2 Hz, 2 H), 2.51–2.72 (m, 4 H), 4.00 (d, J = 8.2 Hz, 2 H), 7.09 (s, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.9 (CH_3), 24.6 (CH_3), 25.8 (CH_2), 35.3 (CH_2), 35.7 (CH_2), 38.7 (C), 80.8 (CH), 129.4 (CH), 130.1 (CH), 140.6 (C), 202 (CO); IR ($CDCl_3$) 3522, 2934, 2858, 1696, 1444 cm^{-1}. Anal. Calcd for $C_{22}H_{32}O_4$ (360.5): C, 73.30; H, 8.95. Found: C, 73.41; H, 8.89. **5(*S**),8(*S**)-Dihydroxy-4,4,9,9-tetramethyl[12]paracyclophane-6,7-dione (25b)**: mp 134–136 °C; R_f 0.09 (silica gel, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.79 (s, 6 H), 0.8 (s, 6 H), 0.82–1.05 (m, 4 H), 1.41–1.82 (m, 4 H), 2.24 (d, H/D, J = 8.0 Hz, 2 H), 2.44–2.63 (m, 2 H), 2.63–2.82 (m, 2 H), 3.94 (d, J = 8.0 Hz, 2 H), 7.10 (s, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.2 (CH_3), 25.0 (CH_2), 25.6 (CH_2), 35.7 (CH_2, double intensity), 39.9 (C), 79.7 (CH), 129.7 (CH), 129.8 (CH), 140.8 (C), 203.5 (CO); IR ($CDCl_3$) 3520, 2934, 2860, 1701, 1505 cm^{-1}. Anal. Calcd for $C_{22}H_{32}O_4$ (360.5); C, 73.30; H, 8.95. Found: C, 73.58; H, 9.82.

6,7-Bis(trimethylsiloxy)-5,6,7,8-diepoxy-4,4,9,9-tetramethyl[12]paracyclophane (28). Using procedure B to prepare **25** we isolated ca. 10% **28** as colorless crystals: mp 112–114 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.13 (s, 18 H), 0.78 (s, 6 H), 1.00 (s, 6 H), 0.68–1.15 (m, 4 H), 1.17–1.48 (m, 2 H), 1.56–1.86 (m, 2 H), 2.38 (s, 2 H), 2.42–2.62 (m, 2 H), 2.62–2.82 (m, 2 H), 7.04 (s, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 1.9 (CSi), 24.2 (CH_3), 26.3 (CH_2), 27.0 (CH_3), 33.6 (C), 35.5 (CH_2), 37.8 (CH_2), 65.6 (CH), 85.7 (COSi), 129.5 (CH), 140.2 (C); HRMS (EI, 70 eV) calcd for $C_{28}H_{48}O_4Si_2$ 504.3091, found 504.3132, m/z (relative intensity) 504.3132 (M^+, 5), 489.2863 ($M^+ - CH_3$, 7), 474.3173 ($M^+ - CO$, 12), 448.3187 ($M^+ - 2CO$, 29), 387.2662 (100).

4,4,9,9-Tetramethyl[12]paracyclophane-5,6,7,8-tetrone (26). To a solution of oxalyl chloride (85 mg, 0.66 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise DMSO (55 mg, 0.7 mmol) under argon at −70 °C. The resulting solution was stirred for 30 min at −50 °C, then **25** (110 mg, 0.305 mmol) in dry CH_2Cl_2 (10 mL) at −40 °C was added. After the solution was stirred for an additional 45 min, triethylamine (200 mg, 2 mmol) was added, the cooling

bath was removed, and the stirring was continued for 2 h. During that time the color changed from orange to red. After part of the solvent was evaporated, the precipitated salts were filtered off and the residue was purified by flash chromatography (silica gel, CH_2Cl_2/CCl_4 (1:1)) to yield 70 mg (64%) of **26** as a red solid. Recrystallization from CH_2Cl_2-pentane afforded red to violet crystals: mp 128 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.18 (s, 12 H), 1.30-1.53 (m, 4 H), 1.62-1.78 (m, 4 H), 2.44-2.62 (m, 4 H), 6.95-7.05 (s, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.4 (CH_3), 28.4 (CH_2), 35.0 (CH_2), 35.4 (CH_2), 47.8 (C), 129.8 (CH), 140.0 (C), 185.3 (CO), 205.4 (CO); IR ($CDCl_3$) 2962, 2928, 2854, 1724, 1699, 1507, 1470, 1456 cm^{-1}; UV (CH_2Cl_2) (λ_{max} (nm), (log ϵ)) 259 (2.83), 264 (2.84), 272 (2.77), 300 sh, 402 (1.77), 507 (1.62); HRMS (EI, 70 eV) calcd for $C_{21}H_{28}O_3$ (M^+ - CO, 1) 328.2094, found 328.2039, calcd for $C_{20}H_{28}O_2$ (M^+ - 2CO, 2) 300.2089, found 300.2093, calcd for $C_{19}H_{28}O$ (M^+ - 3CO, 5) 272.2140, found 272.2137, calcd for $C_{18}H_{28}$ (M^+ - 4CO, 9) 244.2191, found 244.2223, calcd for $C_{17}H_{25}$ (M^+ - 4CO - CH_3, 100) 229.1956, found 229.1949. Anal. Calcd for $C_{22}H_{28}O_4$ (356.5): C, 74.13; H, 7.92. Found: C, 73.81; H, 7.92.

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Supplementary Material Available: Tables of bond lengths, bond angles, some torsional angles, and atomic coordinates of **24**, **25b**, and **26** (13 pages). Ordering information is given on any current masthead page.

Multiple Pathways in the Solvolysis of 1-Adamantyl Fluoroformate†

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Reactions of 1-adamantyl fluoroformate in hydroxylic solvents have been studied. In solvents of high ionizing power and relatively low nucleophilicity, such as 2,2,2-trifluoroethanol-water mixtures, the reactions parallel those of 1-adamantyl chloroformate, and only solvolysis-decomposition reaction is observed. However, differing from the reactions of the corresponding chloroformate, in other solvents appreciable amounts of attack at acyl carbon occur, more than 90% in ≥80% aqueous ethanol. Entropies of activation for attack at acyl carbon are considerably more negative than for solvolysis-decomposition. For the solvolysis-decomposition, a Grunwald-Winstein m value of 0.70 is observed. The k_{Cl}/k_F ratios for solvolysis-decomposition are in the range of 10^4-10^5, suggesting appreciable C-X bond breaking in the transition state of the rate-determining step and arguing against rate-determining formation of a $1\text{-Ad}^+(OCOX)^-$ ion pair. Attack at acyl carbon is analyzed in terms of the two-term Grunwald-Winstein equation, and sensitivities toward changes in nucleophilicity and ionizing power are identical to those for solvolyses of *n*-octyl fluoroformate, which are believed to proceed via a tetrahedral intermediate. For each of the major pathways, selectivities toward the components of binary hydroxylic solvents are reported and discussed.

Introduction

A recently published study[2] of the solvolysis-decomposition of 1-adamantyl chloroformate (1-AdOCOCl) is extended to 1-adamantyl fluoroformate. Fluoroformates have been studied less extensively than chloroformates,[3,4] and the 1-adamantyl ester is unusual in being commercially available; it is a recommended reagent in peptide synthesis.[5]

Chloroformates have usually been found to undergo attack at acyl carbon, but 1-adamantyl chloroformate gave evidence for this only in ethanol, and even there the percentage of the mixed carbonate formed was less than 1%. In a variety of other solvents commonly used in studies of solvolysis reactions, the only products detected were 1-adamantyl chloride from decomposition and 1-adamantanol and/or 1-adamantyl alkyl ether from a solvolysis process accompanied by a loss of carbon dioxide. This pathway was termed the solvolysis-decomposition pathway.[2] The reaction was formulated as proceeding through a 1-Ad^+Cl^- ion pair, formed either by a concerted process involving expulsion of carbon dioxide or via a very unstable $(1\text{-AdOCO})^+Cl^-$ ion pair.

For either a concerted or a stepwise pathway, the carbon-halogen bond is broken in the rate-determining step, and considerably reduced rates are to be expected in the solvolysis-decomposition pathway when the chlorine is replaced by fluorine. For an extreme case, the hydrolysis of triphenylmethyl halides in aqueous acetone,[6] the reactivity ratio favors the chloride over the fluoride by as much as 10^6. For bimolecular attack at acyl carbon, it has been found that fluoroformates usually solvolyze slightly faster than chloroformates.[7-9] Accordingly, the net result of replacing chlorine by fluorine should be a pronounced shift away from solvolysis-decomposition and toward bi-

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