IpcB(OMe)(2-methyl-3-pentyl), 123569-31-3; IpcB(OMe)(3-methyl-2-butyl), 123593-33-9; IpcB(OMe)(cyclopentyl), 123569-32-4; IpcB(2-methyl-1-pentyl)$_2$, 123569-33-5; *i*-PrB(OPr-*i*)(2-methylcyclohexyl), 123569-34-6; *t*-BuB(OPr-*i*)(3-methyl-2-butyl), 123569-35-7; $CH_3CH_2CH{=}CHCH_2CH_3$, 592-47-2; $CH_2{=}CH(CH_2)_6CH_3$, 124-11-8; BuB(3,3-dimethyl-1-butyl)(3-hexyl), 123593-34-0; IpcB(*n*-Bu)(1-hexyl), 123569-36-8; *t*-BuB(cyclopentyl)(1-nonyl), 123569-37-9; *n*-BuB(cyclopentyl)(1-hexyl), 123569-38-0; *n*-BuC(OH)(3,3-dimethyl-1-butyl)(3-hexyl) isomer I, 123569-39-1; *n*-BuC(OH)(3,3-dimethyl-1-butyl)(3-hexyl) isomer II, 123569-91-5; IpcC(OH)(*n*-Bu)(1-hexyl) isomer I, 123569-40-4; IpcC(OH)(*n*-Bu)(1-hexyl) isomer II, 123569-92-6; *t*-BuC(OH)(cyclopentyl)(1-nonyl), 123569-41-5; *n*-BuC(OH)(cyclopentyl)(1-hexyl), 123569-42-6; IpcMeBH, 123569-43-7; Ipc(cyclopentyl)BH, 123569-44-8; Ipc(*s*-Bu)BH, 123569-45-9; *i*-PrBH(4-methyl-2-pentyl), 123569-46-0; *i*-PrBH(2-methyl-3-pentyl), 123569-47-1; *i*-PrBH(2-phenylethyl), 123569-48-2; *i*-PrBH(1-phenylethyl), 123569-49-3; *i*-PrB(2-hexyl)$_2$, 123569-53-9; *i*-PrB(3-hexyl)$_2$, 123569-54-0; *i*-PrB(4-methyl-2-pentyl)$_2$, 123569-55-1; *i*-PrB(2-methyl-3-pentyl)$_2$, 123569-56-2; *i*-PrB(4-methyl-2-pentyl)(2-methyl-3-pentyl), 123569-57-3; *i*-PrB(2-phenylethyl)$_2$, 123569-58-4; *i*-PrB(1-phenylethyl)$_2$, 123569-59-5; *i*-PrB(2-phenylethyl)(1-phenylethyl), 123569-60-8; *n*-BuBH(1-hexyl), 123569-50-6; *n*-BuBH(2-hexyl), 123569-51-7; *n*-BuBH(3-hexyl), 123569-52-8; *n*-BuB(2-hexyl)$_2$, 123569-61-9; *n*-BuB(3-hexyl)$_2$, 123569-62-0; *n*-BuB(4-methyl-2-pentyl)$_2$, 123569-63-1; *n*-BuB(2-methyl-3-pentyl)$_2$, 123569-64-2; *n*-BuB(4-methyl-2-pentyl)(2-methyl-3-pentyl), 123569-65-3; *n*-BuB(2-phenylethyl)$_2$, 123569-66-4; *n*-BuB(1-phenylethyl)$_2$, 123569-67-5; *n*-BuB(2-phenylethyl)(1-phenylethyl), 123569-68-6; *n*-BuBH(4-methyl-2-pentyl), 123569-94-8; *n*-BuBH(2-methyl-3-pentyl), 123569-95-9; *n*-BuBH(2-phenylethyl), 123569-96-0; *n*-BuBH(1-phenylethyl), 123569-97-1; *s*-BuBH(2-hexyl), 123569-98-2; *s*-BuBH(1-hexyl), 123569-99-3; *s*-BuBH(4-methyl-2-pentyl), 123570-00-3; *s*-BuBH(2-methyl-3-pentyl), 123570-01-4; *s*-BuBH(2-phenylethyl), 123570-02-5; *s*-BuBH(1-phenylethyl), 123570-03-6; *s*-BuB(1-hexyl)$_2$, 123569-69-7; *s*-BuB(2-hexyl)$_2$, 123569-70-0; *s*-BuB(3-hexyl)$_2$, 123569-71-1; *s*-BuB(2-hexyl)(3-hexyl), 123569-72-2; *s*-BuB(4-methyl-2-pentyl)$_2$, 123569-73-3; *s*-BuB(2-methyl-3-pentyl)$_2$, 123569-74-4; *s*-BuB(4-methyl-2-pentyl)(2-methyl-3-pentyl), 123569-75-5; *s*-BuB(2-phenylethyl)$_2$, 123569-76-6; *s*-BuB(1-phenylethyl)$_2$, 123569-77-7; *t*-BuBH(2-hexyl), 123570-04-7; *t*-BuBH(3-hexyl), 123570-05-8; *t*-BuBH(4-methyl-2-pentyl), 123570-06-9; *t*-BuBH(2-methyl-3-pentyl), 123570-07-0; *t*-BuBH(2-phenylethyl), 123570-08-1; *t*-BuBH(1-phenylethyl), 123570-09-2; *t*-BuB(2-hexyl)$_2$, 123569-78-8; *t*-BuB(3-hexyl)$_2$, 123569-79-9; *t*-BuB(2-hexyl)(3-hexyl), 123569-80-2; *t*-BuB(4-methyl-2-pentyl)$_2$, 123569-81-3; *t*-BuB(2-methyl-3-pentyl)$_2$, 123569-82-4; *t*-BuB(2-phenylethyl)$_2$, 123569-83-5; *t*-BuB(1-phenylethyl)$_2$, 123569-84-6; IpcBH(1-hexyl), 123570-10-5; IpcBH(2-hexyl), 123570-11-6; IpcBH(3-hexyl), 123570-12-7; IpcBH(4-methyl-2-pentyl), 123570-13-8; IpcBH(2-methyl-3-pentyl), 123570-14-9; IpcBH(2-phenylethyl), 123570-15-0; IpcBH(1-phenylethyl), 123570-16-1; IpcB(1-hexyl)$_2$, 123569-85-7; IpcB(2-hexyl)$_2$, 123569-86-8; IpcB(3-hexyl)$_2$, 123569-87-9; IpcB(2-hexyl)(3-hexyl), 123569-88-0; IpcB(4-methyl-2-pentyl)$_2$, 123569-89-1; IpcB(2-methyl-3-pentyl)$_2$, 123569-90-4; IpcB(2-phenylethyl)$_2$, 123593-35-1; IpcB(1-phenylethyl)$_2$, 123593-36-2; IpcB(2-phenylethyl)(1-phenylethyl), 123593-37-3; $MeBH_2{\cdot}SMe_2$, 84470-72-4; $t\text{-}BuBH_2{\cdot}SMe_2$, 84280-41-1; 1-hexene, 592-41-6; 3,3-dimethyl-1-butene, 558-37-2; 2-methyl-1-pentene, 763-29-1; 2-ethyl-1-butene, 760-21-4; 2,3-dimethyl-1-butene, 563-78-0; styrene, 100-42-5; *trans*-2-hexene, 4050-45-7; *trans*-4-methyl-2-pentene, 674-76-0; cyclopentene, 142-29-0; 1-methylcyclopentene, 693-89-0; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; α-pinene, 80-56-8; 3-methyl-1-butene, 563-45-1; 2-methyl-2-butene, 513-35-9; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7; 3-hexanol, 623-37-0; 4-methyl-2-pentanol, 108-11-2; 2-methyl-3-pentanol, 565-67-3; 2-phenylethanol, 60-12-8; 1-phenylethanol, 98-85-1.

Supplementary Material Available: Mass, IR, and ^{13}C NMR spectra for selected compounds (25 pages). Ordering information is given on any current masthead page.

Trispiro[2.1.2.1.2.1]dodecane-4,8,12-trione and Other Oligomers of Carbonylcyclopropane. The Organozinc Route

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1-Bromocyclopropanecarboxylic acid (**8**) and its chloride (**9**) were prepared from γ-butyrolactone on a 20–100-g scale. Dehalogenation of **9** with zinc–copper couple in acetonitrile gave not only the known dispiro[2.1.2.1]octane-4,8-dione (**3**) but also the aesthetically pleasing title compound **10** and 6-cyclopropylidene-5-oxaspiro[2.3]hexan-4-one (**11**) as well as tetracyclic α-alkylidene-γ-butyrolactone **12**, i.e., 3-(oxodispiro[2.1.2.1]octan-4-ylidene)tetrahydro-2-furanone. "Zinc carbon enolate" **13a** is considered to be an important intermediate en route to **10** in solvent acetonitrile. The X-ray crystal structure of **10** shows the molecule to be nearly planar with very short distal cyclopropane carbon–carbon bonds [1.437 (4)–1.452 (4) Å].

Carbonylcyclopropane (other names, dimethyleneketene or cyclopropylidenemethanone) (**2**) is a reactive ketene that has been generated by Brown and his co-workers when they submitted the spiroannulated Meldrum acid **1** to flash vapor thermolysis (FVT).[1a] Carbonylcyclopropane has

† Née U. Bültel.
‡ Née A. Kütz.
§ Née E. Tiller.
‖ X-ray analysis of **10**.
⊥ X-ray analysis of **12**.

(1) (a) Baxter, G. J.; Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J. *Tetrahedron Lett.* **1975**, 4283. (b) Brown, R. F. C. *Chem. Brit.* **1987**, 1189. See also: Brown, R. F. C. *Chem. Brit.* **1988**, 770. (c) See also: Ripoll, J. L. *Tetrahedron* **1977**, *33*, 389. Bock, H.; Hirabayashi, T.; Mohmand, S. *Chem. Ber.* **1981**, *114*, 2595.

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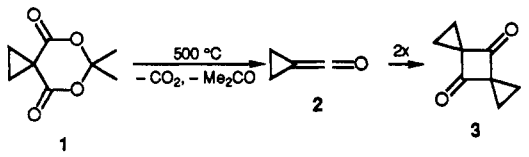
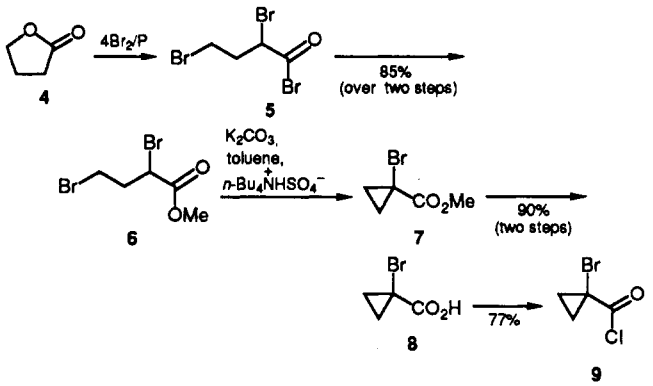
been suggested to be not linear, but marginally bent away from the symmetrical conformation.[1b] It was found to dimerize to dispiro[2.1.2.1]octane-4,8-dione (3) below 0 °C.[1a] We thought it of interest to generate 2 by an organometallic route, using zinc and 1-bromocyclopropanecarbonyl chloride (9). During these studies we have found two new cyclic trimers and another, hitherto unknown dimer of 2.[2] The compounds are structurally fascinating and of preparative interest. The formation of the new products is proposed to implicate organozinc intermediates rather than free carbonylcyclopropane (2).



1 2 3

Results

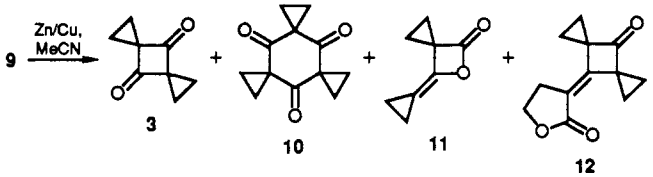
Parent 1-bromocyclopropanecarbonyl chloride (9) was prepared by a simple and efficient procedure starting with inexpensive γ-butyrolactone (4), which after three steps gave α-brominated ester 7. The intramolecular cyclization



4 5 6 7 8 9

of 6 to 7 worked well under two-phase, solid–liquid-phase conditions. In practice, >200 g of dibromo ester 6 was used, and the resulting monobromo ester 7 was not isolated, but saponified directly, giving 1-bromocyclopropanecarboxylic acid (8), mp 78–80 °C,[3] after distillation, in quantities of >80 g per batch.

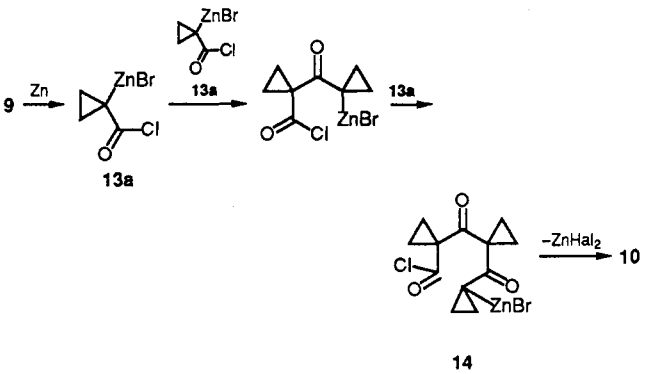
The zinc-induced dehalogenation of 9 was carried out under a variety of conditions. With zinc in *tetrahydrofuran*, the known cyclic dimer 3[1] was the main product. However, when we switched to *acetonitrile* as a solvent, three new ring systems were formed, including trimer 10.



3 10 11 12

The formation of 10 from 9 could be followed by integration of the resolved 200-MHz ^{1}H NMR spectrum of the crude product (singlet at δ 1.98). However, even after various precautions had been taken, the preparation of 10 proved to be erratic, and, occasionally, triketone 10 was *not formed at all*. We therefore standardized the conditions for the preparation and workup of 10, 11, and 12 (Table I), adding neat acid chloride 9 to a suspension of activated zinc in acetonitrile under various conditions.

Scheme I



13a 14

Discussion

Inspection of Table I shows that rapid addition of the acid chloride 9 to activated zinc produced dimer 3 almost exclusively (entry 1). Triketone 10 was formed only as a trace. Conversely, *slow* addition using a perfusor at 40–50 °C without ultrasound gave the highest percentage and isolated quantity of cyclic trimer 10 (entry 14). Doubling the quantity of acetonitrile reduced the formation of 10 (entry 12). α-Alkylidene-γ-butyrolactone 12 was formed in the absence of sonication (entries 3 and 14). Addition of $ZnCl_2$ had no noticeable effect (entry 10), and addition of NEt_3 allowed isolation of only cyclic diketone 3 (entry 11). The new, strained tricyclic β-lactone 11 was sensitive to workup with nucleophiles [aqueous NH_3 (entries 1–3), NEt_3 (entry 11), and H_2O (entry 6)] and had to be isolated without delay under strictly nonaqueous conditions of workup. We also observed that sonication of the reaction mixture, which is known to produce a highly reactive form of zinc, favored formation of 11 (entries 7–10, 12, and 13).

As a simple mechanistic sequence, we envisage α-(chlorocarbonyl)cyclopropane zinc bromide (13a), i.e., a "zinc carbon enolate", as an intermediate en route to 10 (Scheme I). The organozinc species 13a is nucleophilic, by virtue of the carbon–zinc bond, and because of the chlorocarbonyl group, it is also electrophilic. Since both acetonitrile and zinc are mandatory for the formation of 10, a correct balance of nucleophilicity and electrophilicity of the organozinc intermediates is probably important for obtaining 10. In order to corroborate the intervention of organozinc intermediates in the formation of the three compounds 10–12, we have repeated the flash vapor thermolysis (FVT) of 1 and isolated only 3.[1a,b] Since free carbonylcyclopropane (2) has previously been clearly implicated on FVT of 1,[1a,b] this intermediate is probably also generated during the zinc-induced reaction in solvent tetrahydrofuran, but no so—or only partially—in acetonitrile. The structure of the second carbonylcyclopropane trimer 12 was not obvious from a consideration of spectroscopic data. In the ^{13}C NMR spectrum two singulets at 110.4 ppm and at 158.8 ppm suggested a tetrasubstituted carbon–carbon double bond with the possibility that the signal at 158.8 ppm was due to strain and intervention of a heteroatom. Interestingly, the IR spectrum showed three sharp, intense peaks at 1790, 1740, and 1690 cm^{-1}. The structure of 12 was eventually determined by X-ray

(2) For previous papers in this series, see: Hoffmann, H. M. R.; Wulff, J. M.; Kütz, A.; Wartchow, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 17. Wulff, J. M.; Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 605. Hoffmann, H. M. R.; Walenta, A.; Eggert, U.; Schomburg, D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 607. Hoffmann, H. M. R.; Geschwinder, P. M.; Hollwege, H.-P.; Walenta, A. *Helv. Chim. Acta* **1988**, *71*, 1930.

(3) Barnier, J. P.; Rouesseau, G.; Conia, J. M. *Synthesis* **1983**, 915. Bruylants, P. *Bull. Soc. Chim. Belg.* **1923**, *32*, 358; *Chem. Abstr.* **1924**, *18*, 975.

Table I. Products of the Zinc-Induced Dehalogenation of 9[a]

entry	9 educt, g	addtn time of neat educt, min	activtd zinc, equiv	crude product (after column filtrt) g	%	3 mg	%	10 mg	%	11 mg	%	12 mg	%	remarks	total yield after chromatography, %
1	8	10	3	1.2	40.5	*b*	*b*							ca. 40–90 °C, aq NH_3 workup	
2	8	20	3	1.1	37	240	8	100	3.4					ca. 40–90 °C, aq NH_3 workup	11.4
3	8	30	3	1.41	47.6	340	11.5	250	8.5			300	10	ca. 40–90 °C, aq NH_3 workup	30
4	7.5	10	3	1.36	49	390	14	100	3.6	20 impure				ultrasound, ca. 20 °C bath temp	17.6
5	8	30	3	1.52	51.4	380	12.8	280	9.5	30 impure				ultrasound, ca. 20 °C bath temp	
6	8	30	3	0.82	27.7	280	9.5	100	3.4	30	1			ultrasound, H_2O/CH_2Cl_2 workup	13.9
7	5	60	4.4	0.93	14.6	270	14.6	170	9.2	130	7	traces		ultrasound, H_2O/CH_2Cl_2 workup	30.8
8	4	300	6	1.1	74.3	200	13.5	210	14.2	270	18.2			ultrasound, nonaqueous workup by removal of MeCN and chromatography	45.9
9	4	210[c]	6	1.0	67.5	390	26.4	160	10.8	190	12.8			ultrasound, nonaqueous workup by removal of MeCN and chromatography	50
10	4	300	6	1.0	67.5	260	17.6	180	12.2	190	12.8			$ZnCl_2$ added, ultrasound	42.6
11	2	150	6	0.25	30	120	16							NEt_3 added, ultrasound	16
12	3	180	6	0.65	59	220	19.8	110	9.9	130	11.7			ultrasound, double quantity of solvent	41.4
13	5	300	6	1.4	75	380	20.5	300	16.2	310	16.8			ultrasound, ca. 20 °C bath temp	53.5
14	5	300	3	1.8	97	330	17.8	370	20			200	10.8	no ultrasound, ca. 40–50 °C bath temp	48.6

[a] In the ultrasound experiments the zinc was preactivated by sonication in MeCN for 30 min (entries 3–14). [b] ^1H NMR of crude products shows dimer only. [c] Stirred for a further 150 min.

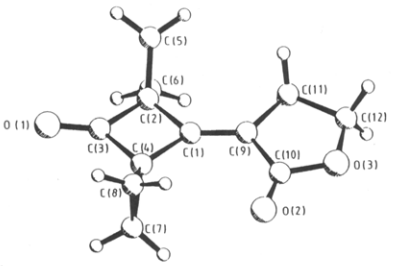


Figure 1. SCHAKAL plot of tetracyclic α-alkylidene-γ-butyrolactone **12**.

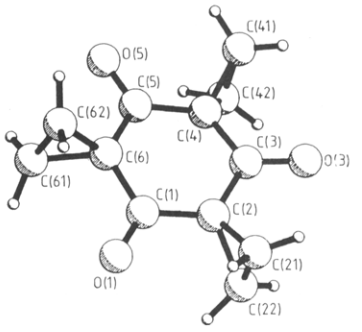
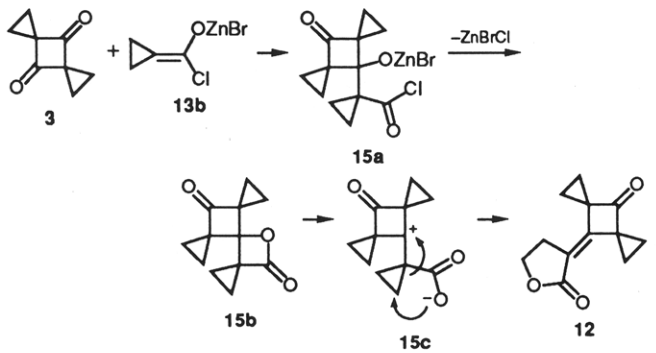


Figure 2. PLUTO plot of triketone **10**.

diffraction, which revealed a strained α-alkylidene-γ-butyrolactone (Figure 1).

How is tetracyclic α-alkylidene-γ-butyrolactone **12** being formed? It is noticeable that **12** was obtained only under thermal activation (entries 3 and 14) and when the acid chloride **9** was added over a period of 30 min and longer. Presumably, lactone **12** arises from diketone **3**. Nucleophilic attack of zinc enolate **13b** at the carbonyl function and subsequent expulsion of zinc halide affords spirolactone **15b** as an intermediate, which is highly strained and, under the influence of zinc salt as a Lewis acid, is opened to zwitterion **15c**. A second opening, in this case of the external cyclopropylmethyl cation fragment to a homoallyl cation and nucleophilic intramolecular trapping by carboxylate, yields lactone **12**.

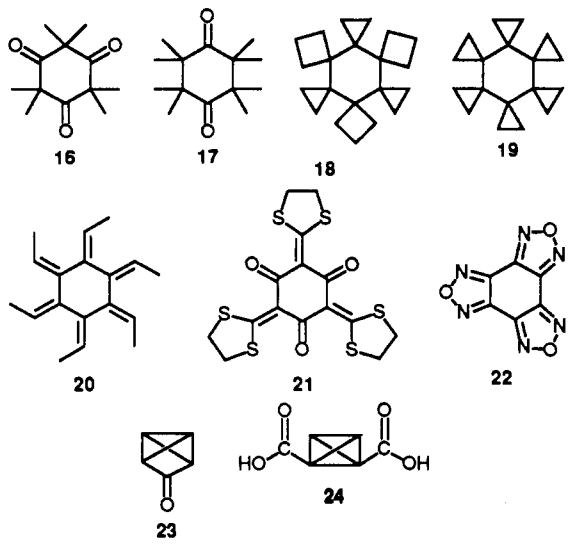


X-ray Crystal Structure of 10

Trispirotriketone **10** is an aesthetically appealing molecule of potential D_{3h} symmetry. Its structure was first deduced by spectroscopy (^1H NMR, ^{13}C NMR, IR, MS; see Experimental Section). The X-ray analysis shows that the six-membered ring is almost flat (cf. PLUTO plot, Figure 2). The intraannular torsion angles (−10.9°, 14.0°, −5.0°, −7.3°, 10.4°, −1.1°) have an absolute sum of only 48.7°. By comparison **16**–**20** (Chart I) have torsion angle sums for the six-membered ring of 192° (boat),[4] 272.5°,[5] 318°,[6] 324°,[7]

(4) Hoffmann, H. M. R.; Hursthouse, M. B.; New, L. *Tetrahedron* **1981**, *37*, 1967.
(5) Hoffmann, H. M. R.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1976**, *98*, 7449.

Chart I



and 276.8° [8] (all chairs). The driving force for this flattening in **10** is the conjugative interaction between each spirocyclopropyl ring and a pair of electron-withdrawing geminal carbonyl substituents.[9] The flattened conformation permits each carbonyl to adopt the favored cis-bisected conformation with respect to *both* adjacent rings. The O=C—C—X angles (X is the midpoint of the distal cyclopropyl bond) range from 1.8 to 15.5° in **10**, all well within the range for highly effective conjugative orbital overlap.[9] Any puckering of **10** toward a boat or chairlike six-membered ring would destroy the concerted conjugative system.

These dominant electronic interactions have interesting effects upon the bond lengths and valence angles in **10**. The distal cyclopropyl bond lengths 1.437 (4)–1.452 (4) Å are amongst the shortest recorded in a precise ($R \leq 0.070$), nondisordered crystal structure of "free" cyclopropane.[10] By comparison the distal bonds in two independent molecules of cyclopropane-1,1-dicarboxylic acid[11] are 1.456 (5) and 1.468 (5) Å; in each molecule one of the COOH carboxyls is cis-bisected and the other trans-bisected with respect to the ring. There are a few distal cyclopropane bonds that *are* shorter or comparable to those in **10** and that occur in structures of good precision. However, they all contain the highly strained bicyclo[1.1.0]butane framework[12] within substructures of type **23** or **24** where bicyclobutane bridge bonds of 1.417 (3),[13] 1.416 (2),[14] 1.443 (3),[15] and 1.451 (2) Å[16] are found.

Within the six-membered ring of **10** the valence angles are all within 119.7 ± 1.2° and add to a benzene-like 718.1°. This may be contrasted to mean valence angles of 111.5 (5)° and 114.1 (1)° in the chairlike rings of **19**[7] and **20**.[8] More importantly the bond lengths in the six-membered ring of **10** range from 1.469 (4)–1.482 (4) Å with a mean of 1.475 (4) Å. This may be contrasted with mean values of 1.521 (8),[4] 1.526 (4),[6] 1.514 (4),[7] and 1.494 (3) Å[8] in **16**, **18**, **19**, and **20**, respectively. The value for **10** is indeed typical for Cp—C=O conjugation[9] and is at the lower end of the range [mean = 1.486 (2) Å] cited[17] for 105 such bond lengths.

The introduction of the three vinylic cyclopropyl carbons into the cyclohexane-1,3,5-trione ring of **16** has, therefore, radically altered the conformation and geometry compared with those exhibited by six-membered carbocycles in which each C sp^2 atom carries an exocyclic double bond. In general, such rings (e.g., **21**[18] and **22**[19]) *are* fully conjugated and flat, with X=C—C=X torsion angles close to 0°, internal valence angles close to 120°, and short single bond lengths typical of highly conjugated systems. Thus C–C in **21** and **22** average to 1.452 (6)[18] and 1.435 (9) Å.[19] The loss of resonance stabilization in **20**, where steric overcrowding forces a puckered conformation,[8] is evidenced by the "anomalous" geometry of the six-membered ring [mean bonds, angles and torsion angles of 1.494 (3) Å, 114.1 (1)°, and 46.2 (1)°].

The X-ray structure of **10**, therefore, provides an unequivocal example of the strength of the cyclopropyl–carbonyl conjugative interaction and provides more proof of the vinylic character of the cyclopropane ring,[20] which must also contribute to the low IR carbonyl stretching frequency of 1668 cm^{-1}.

In summary, the new small ring systems described by us are simple and of intrinsic mechanistic and structural interest. As we shall show they are also valuable in synthesis.

Experimental Section

Methyl 2,4-Dibromobutanoate (6). A 500-mL, three-necked flask was charged with γ-butyrolactone (100 g, 89.3 mL, 1.16 mol) and red phosphorus (13.6 g, 0.44 mol) under N_2 and cooled to −10 °C. Bromine (200 g, 62.5 mL, 2.43 mol) was dropped in at a rate that kept the reaction temperature below 30 °C. After the reaction had slowed down, external cooling was removed and a second portion of bromine (195 g, 61 mL, 2.38 mol) was dropped in, the temperature rising to 40–50 °C. The reaction mixture was stirred for 3 h at 80 °C and cooled to −5 °C and methanol (100 mL) was slowly dropped in. The mixture was distributed between diethyl ether (100 mL) and water (100 mL), and the aqueous phase was discarded. The organic phase was washed with a saturated solution of $NaHCO_3$ and dried ($MgSO_4$), and the solvent was removed on a rotary evaporator, giving crude **6**, which was purified by distillation under reduced pressure, bp 80–85 °C/0.1 Torr. Yield of **6**: 265.1 g (88%); IR (CCl_4) 2980 (m), 1750 (vs, C=O), 1280 (s), 1165 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.4–2.6 (m, 2 H), 3.54 (t, J = 6.0 Hz, 2 H), 3.8 (s, 3 H), 4.52 (t, J = 7.0 Hz, 1 H); mass spectrum, m/e (relative intensity) 260 (0, M^+), 230 (2), 228 (4), 226 (3), 202 (6), 200 (11), 198 (7), 153 (98), 151 (100).

Methyl 1-Bromocyclopropanecarboxylate (7). K_2CO_3 (243.2 g, 1.76 mol) and n-Bu_4NHSO_4 (13.74 g, 0.04 mol) were mixed with dibromo ester **6** (208 g, 0.8 mol) in toluene (300 mL). The suspension was stirred for 40 h at 80 °C. After being cooled down to room temperature, the mixture was filtered with suction through a Büchner funnel and the filtercake was washed several times with ether. The resulting filtrates were collected and used without further purification in the next step. A small purified

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sample was submitted to spectroscopy: IR ($CHCl_3$) 1720 (vs, C=O), 1320 (vs), 1140 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37–1.44 (m, 2 H), 1.65–1.72 (m, 2 H), 3.75 (s, 3 H); mass spectrum, *m/e* (relative intensity) 179 (97, M^+), 177 (100), 149 (53), 147 (56), 121 (35), 119 (35), 99 (18).

1-Bromocyclopropanecarboxylic Acid (8). $KOBu^t$ (195.5 g, 1.76 mol) was suspended in ether. Water (15.9 mL) was added and the mixture was cooled to 0 °C. The solution of **7** in toluene/ether was stirred in, and the mixture was stirred for a further hour at 0 °C. The mixture was treated with ether and extracted five times with a saturated aqueous solution of $NaHCO_3$. The united aqueous phase was acidified with half-concentrated aqueous HCl and extracted with ether (5×). The united organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator, giving a yellow oil or a yellow-colored solid. Sublimation (Kugelrohr, 100 °C/0.1 Torr) gave **8** (83 g, 63% with respect to dibromo ester **6**); mp 78–80 °C.[3] The spectroscopic data agreed with those in ref 3.

1-Bromocyclopropanecarbonyl Chloride (9). **8** (30 g, 0.18 mol) was stirred with $SOCl_2$ (50 mL) for 15 h at room temperature. The excess of $SOCl_2$ was distilled off at normal pressure and the residue was fractionated at reduced pressure (ca. 0.5 Torr). The fraction with bp 38 °C was pure (21 g, 61%): IR (CCl_4) 1780 (vs, C=O), 1260 (m), 1050 (m), 955 (m), 930 (m), 905 (m), 645 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59–1.94 (m, 2 H), 1.92–2.17 (m, 2 H); mass spectrum, *m/e* (relative intensity) 183 (22, M^+), 181 (17), 148 (97), 146 (100), 121 (39), 119 (39).

Trispiro[2.1.2.1.2.1]dodecane-4,8,12-trione (10). A 50-mL three-necked flask equipped with reflux condenser and $CaCl_2$ tube, thermometer, and septum (which was connected to a perfusor) was charged with zinc powder (5.4 g, 80 mmol) and cuprous chloride (75 mg, 0.8 mmol), which were suspended in dry acetonitrile (7.3 mL). The mixture was stirred and heated to 40 °C. Acid chloride **9** (5 g, 27.5 mmol) was added during 5 h with the perfusor. After completed addition, the mixture was stirred for 1 h. The acetonitrile was evaporated and the residue was subjected to column filtration (silica gel, CH_2Cl_2). The crude product thus obtained was chromatographed (silica gel, light petroleum/ether 2:1). The three products **10**, **3**, and rearranged **12** are eluted in this sequence. After collection of diketone **3**, the lactone **12** is eluted with ether. Triketone **10** (370 mg, 20%) was isolated: mp 143–145 °C; IR (KBr) 3120 (w), 3020 (w), 1668 (s, C=O), 1358 (s), 1110 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.98 (s); ^{13}C NMR ($CDCl_3$) δ 29.62 (6 CH_2), 40.68 (3 spiro C), 202.22 (3 C=O); mass spectrum, *m/e* (relative intensity) 204 (17, M^+), 203 (83), 202 (100), 188 (37), 174 (47).

X-ray Analysis of 10. Crystals of **10**, obtained by column chromatography as described above, have monoclinic symmetry, space group $P2_1/c$. The unit cell, which has the parameters a = 8.550 (2), b = 15.665 (6), and c = 8.408 (2) Å, and β = 118.49 (3)°, contains 4 molecules, yielding a calculated density of 1.370 g/cm^3. The data were collected at 293 K on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo K_α radiation (λ = 71.07 pm) in the θ–2θ mode in the range $3° \le 2\theta \le 50°$ at a scan speed between 2.93° and 29.30°/min depending on the intensity of the reflection.

The data were corrected for Lorentz and polarization effects, but no absorption correction was made (μ = 0.058 mm^{-1}). The structure was solved by direct methods and difference-Fourier syntheses. The hydrogen atom positions were determined from difference-Fourier syntheses and refined independently together with isotropic temperature factors. The refinement using 1355 out of 1746 measured independent reflections ($F \ge 2.5\sigma(F)$) converged at R = 0.048. A final difference map displayed no electron density higher than 0.21 × 10^{-6} e/pm^3. The program SHELX-76[21] and our own programs were used. Complex atom scattering factors[22] were employed.

6-Cyclopropylidene-5-oxaspiro[2.3]hexan-4-one (11). This compound was formed preferentially under sonication (Table I, e.g., entry 13) and isolated without delay. Chromatography on silica gel (light petroleum/ether 2:1) gave **11** as first fraction and then **10** and **3**, in this sequence. Lactone **11**: white solid, mp 59–60 °C; IR ($CHCl_3$) 1890 (s, combination band of 875 and 990 cm^{-1}, possibly enhanced by Fermi resonance), 1800 (vs), 1150 (s), 1125 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18–1.29 (m, 2 H), 1.29–1.41 (m, 2 H), 1.44–1.53 (m, 2 H), 1.55–1.65 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 1.9, 2.7, 12.3 (3 t, cyclopropane CH_2), 34.18 (s, spiro C), 86.8 (s, $(CH_2)_2C$=C), 139 (s, $(CH_2)_2$C=*C*), 173.3 (s, C=O); mass spectrum, *m/e* (relative intensity) 136 (6.25, M^+), 79 (52), 68 (64), 56 (100); exact mass calcd for $C_8H_8O_2$ 136.0524299, found 136.0523779. Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.31; H, 5.90.

3-(8-Oxadispiro[2.1.2.1]octan-4-ylidene)tetrahydro-2-furanone (12): white solid, mp 114–116 °C; IR (KBr) 1790 (vs), 1740 (vs) 1690 (vs), 1335 (s), 1235 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (m, 2 H), 1.78 (m, 4 H), 2.4 (m, 2 H), 2.82 (t, J = 7.5 Hz, 2 H), 4.4 (t, J = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.0 and 20.6 (2 t, cyclopropane C), 24.4 (t, -*C*$H_2$$CH_2O$), 45.2 and 47.1 (2 S, spiro C), 65.9 (t, -CH_2*C*H_2O), 110.4 (s, *C*=CO), 158.8 (s, C=*C*O), 169.8, 213.4 (2 s, C=O); mass spectrum, *m/e* (relative intensity) 204 (21, M^+), 189 (70), 176 (39), 161 (35), 91 (100); exact mass calcd for $C_{12}H_{12}O_3$ 204.07864, found 204.07855. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.49; H, 6.00.

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Supplementary Material Available: Tables of X-ray data (Tables 2–8) and X-ray analysis of **12** (7 pages). Ordering information is given on any current masthead page.

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