Novel Synthesis of Five- and Six-Membered Spiro γ-Lactones in Rigid Bicyclic Systems[1]

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The reaction of bis(bromomagnesio)alkanes with bridged tricyclic *endo*- and *exo*-dicarboxylic anhydrides and their dihydro derivatives provides a general and versatile route to corresponding tricyclic spiro γ-butanolides. Further extension of this methodology to the dianhydride of bicyclo[2.2.2]octene showed appreciable regioselectivity. The subsequent transformatioin of spiro γ-lactones into 4-spiro-2-butenolides by retro-Diels–Alder reaction has provided a simple and convenient synthesis of these molecules. Proton and ^{13}C NMR spectra are reported for most of the compounds.

We have previously reported a new synthetic approach for the preparation of spiro γ- and δ-lactones in monocyclic bicyclic and fused tricyclic systems.[2] This methodology, based on the reaction of α,ω-diprimary di-Grignard reagents with cyclic or polycyclic anhydrides, provides the appreciable advantage of retaining the initial stereochemistry of the substrate unchanged.

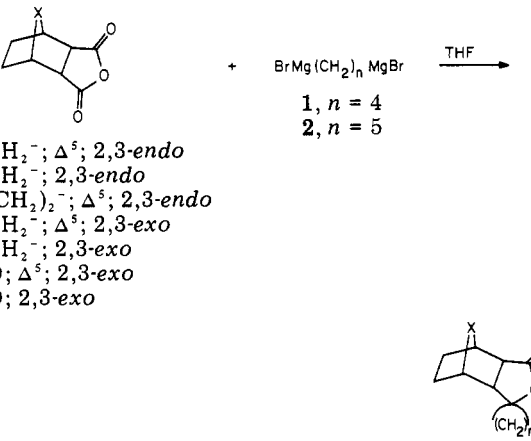
In order to demonstrate the versatility of this method, we now to report that the reactions of α,ω-bis(bromomagnesio)alkanes can be extended to more complex compounds such as the bridged endo and exo bicyclic systems **3–9** and that they provide a novel approach into the series of bridged tricyclic spiro γ-lactones[3] as is outlined in Scheme I. As described below, the *endo*- and *exo*-bicyclo[2.2.1]heptane derivatives have now also been investigated, and we show that they give a good yield of the corresponding lactones.

The above lactones as well as those of unsaturated skeletons which we are presenting in this paper have not been previously reported, although the starting anhydrides are easily obtained by Diels–Alder[3] reactions and by subsequent transformations.[4-6] Reactions of 1,4-bis(bromomagnesio)butane and 1,5-bis(bromomagnesio)pentane with bridged tricyclic anhydrides occurred as described previously when an equimolar ratio of di-Grignard reagent and dicarboxylic anhydride was used.[2] Under the same experimental conditions the reactions with 1,4-bis(bromomagnesio)butane gave the corresponding spiro γ-lactones in higher yields than did the reactions with 1,5-bis(bromomagnesio)pentane. These differences have been found for all cases of five-membered spiroannelation. However, for both spiroannelations the yield of lactones is good to excellent, even for the saturated anhydrides.

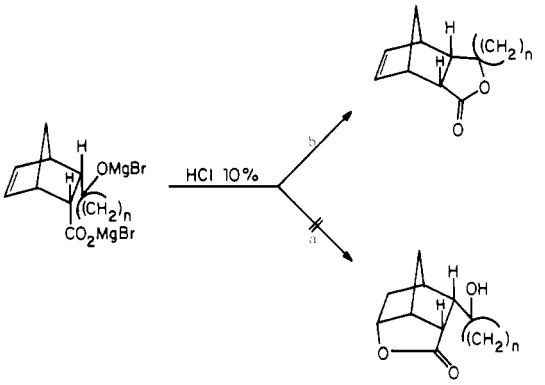
As is shown in Table I, the hydrogens in positions 5 and 6 of saturated anhydrides **4**, **8**, and **9** do not play any important role in the spiroannelation process. Furthermore, the reactions with the two unsaturated *endo*-dicarboxylic anhydrides **3** and **5** showed an important chemiospecificity relative to the two expected pathways of lactonization. Thus we noticed that only spiro lactones corresponding to the initial skeleton were obtained (pathway b). In other words the transannular process (pathway a) which would provide the isomeric lactone does not occur after hydrochloric hydrolysis as was observed in other *endo*-bridged compounds in the presence of acetic acidic[7] (Scheme II).

Therefore, our results are consistent for all three series of substrates. The reaction of organodimagnesium compounds with dicarboxylic anhydrides yield the same type of spiro γ-lactonic compounds as was previously found in the case of fused bicyclic anhydrides. The above results together with others indicate that the scope of spiroannelation is indeed rather limited.

Scheme I



Scheme II



(1) Canonne, P.; Bélanger, D.; Lemay, G. "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta GA; American Chemical Society: Washington, DC, 1981; ORGN 80.

(2) (a) Canonne, P.; Bélanger, D. *J. Chem. Soc., Chem. Commun.* **1980**, 125. (b) Canonne, P.; Bélanger, D.; Lemay, G.; Foscolos, G. B. *J. Org. Chem.* **1981**, *46*, 3091. (c) Canonne, P.; Lemay, G.; Bélanger, D. *Tetrahedron Lett.* **1980**, 4167.

(3) See ref 16 for a discussion of general methods of spiro lactone formation, and references quoted therein.

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(5) Craig, D. *J. Am. Chem. Soc.* **1951**, *73*, 4889.

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Scheme III

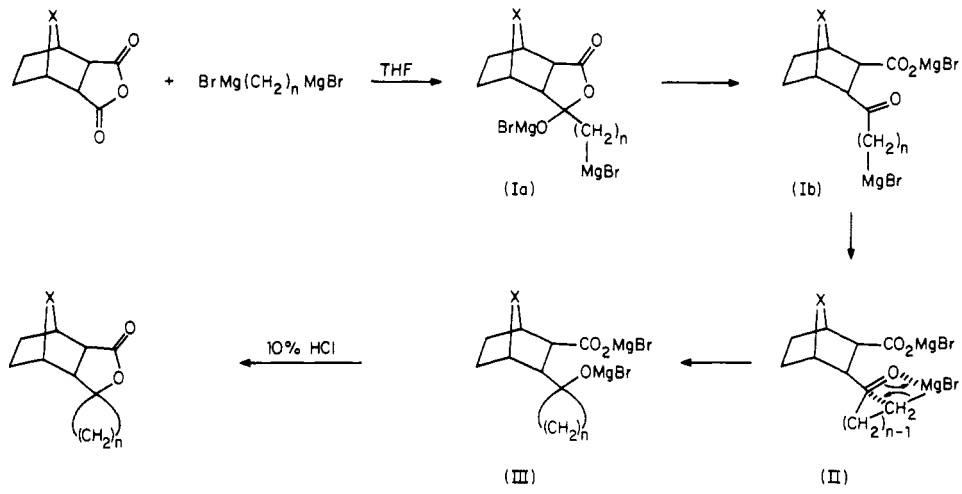

Table I. Spiro Lactones from the Reaction of Bis(bromomagnesio)alkanes with Cyclic Dicarboxylic Acid Anhydrides

	$BrMg(CH_2)_4MgBr$		$BrMg(CH_2)_5MgBr$	
anhydride	product	yield, %	product	yield, %
3	11	85	12	75
4	13	84	14	74
5	15	85	16	75
6	17	90	18	80
7	19	90	20	80
8	21	85	22	75
9	23	88	24	78

In conclusion, the reaction yields good results even in the presence of a large excess of di-Grignard reagents and without strict temperature control.

Indeed, we found no evidence of the presence of diols and ketols either by chromatography or by ^1H NMR and IR spectroscopy, which would indicate that the carboxylate group was not attacked by the reagents.[8]

Consequently, in the formation of spiro γ-lactones we propose that the reaction process should occur as is shown in Scheme III. Initially, the attack of the organodimagnesium gives the lactol Ia which in turn is rapidly transformed into keto carboxylate Ib, as is supported by IR spectroscopy data.[9] The intramolecular attack gives the cyclic alkoxy carboxylate which provides the corresponding spiro γ-lactone in the presence of HCl. With these two Grignard reagents we did not find any compound corresponding to an attack of the organomagnesium part of Ib with another molecule of dicarboxylic anhydride by an intermolecular process.

This easy one-step transformation of bridged bicyclic anhydrides into five- and six-membered tricyclic spiro γ-lactones suggests that dispiro di-γ-lactones might also be obtained from the corresponding dianhydrides. Indeed, as expected, treatment of the commercially available bicyclo[2.2.2] tetracarboxylic dianhydride **10** with both bis(bromomagnesio)alkanes gave two isomeric dispiro di-γ-lactones with pronounced regioselectivity, as is summarized in Scheme IV. The sterically less favored compounds **26** and **28** are found to be minor products as was confirmed by ^1H NMR spectroscopy. These results confirm our previous observations that the reaction of di-Grignard reagents is sensitive to the steric effect.[2] Consequently, the alternate easier route provides preferentially the isomeric lactones **25** and **27** as major products.

Also in these reactions we observed that the 1,4-bis(bromomagnesio)butane produces the corresponding lactones in better yields than those for its homologue. It was also established that no other competitive lactonization takes place even in the presence of acetic acid. More precisely, we did not find any isomeric lactone corresponding to a transannular lactonization between the carboxylic group in position 3 and the hydroxyl group in position 10 as shown by the data summarized in Scheme IV.

Finally, we report another very interesting aspect of our work which illustrates the further transformation of the obtained bridged spiro lactones into spiro butenolides.

(8) The yield reported in Table I is given after purification by fractional distillation or by recrystallization, as stated in the Experimental Section. The analytical data confirmed the assigned structures.

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Scheme IV

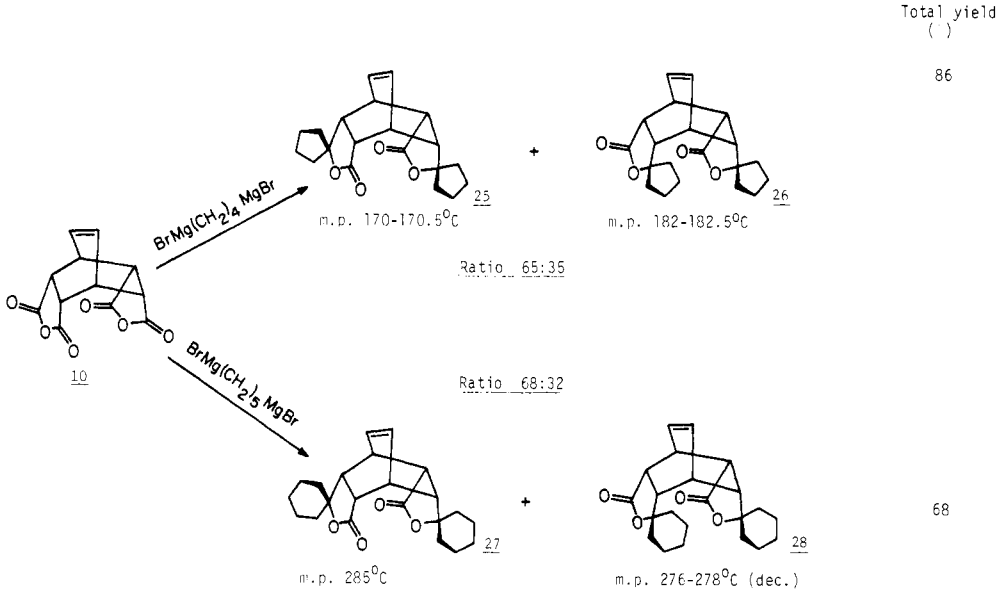
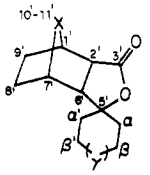


Table II. ^{1}H NMR Comparative Data for Spiro Lactones in Bicyclo[2.2.1]hept-5-ene and -[2.2.2]oct-5-ene Series



compd	δ(hydrogen) [a]				coupling constants, Hz			
	1'-H	2'-H	6'-H	7'-H	$J_{1',2'}$	$J_{2',6'}$	$J_{6',7'}$	$\Delta\nu/J$
11 (endo)	3.27	3.39	2.87	3.07	4.5	8.5	4	5.5
12	3.23	3.41	2.71	3.04	5	8.5	3.5	7.5
15	3.07	3.01	2.44	2.76	4	9.5	2	5.4
16	3.05	2.99	2.21	2.72	4	9	2	7.8
17 (exo)	3.27	2.79	2.26	3.01	<1	8	<1	6.0
18	3.25	2.79	2.07	3.00	<1	8	<1	8.1
21 (7-oxa)	5.27	2.96	2.43	5.12	0	7.5	0	6.3
22	5.23	2.92	2.21	5.14	0	7.5	0	8.5

[a] All spectra were recorded in $CDCl_3$, 50 mg of sample/0.5 mL. [b] Data related to H'-2 and H'-6.

Table III. ^{1}H NMR Comparative Data for Spiro Lactones in Bicyclo[2.2.1]heptane Series

compd	δ(hydrogen) [a]				coupling constants, Hz			
	1'-H [b]	2'-H	6'-H	7'-H	$J_{1',2'}$	$J_{2',6'}$	$J_{6',7'}$	$\Delta\nu/J$
13 (endo)	2.63	3.10	2.56	2.42	6	10	4.5	4.9
14	2.62	3.07	2.39	2.39	6	11	4.5	5.5
19 (exo)	2.66	2.71	2.16	2.43	<1	8	<1	6.3
20	2.61	2.70	1.94	2.43	<1	9	<1	8.5
23 (7-oxa)	4.82	2.96	2.42	4.72	0	8	0	6.0
24	4.82	2.95	2.21	4.77	<1	8	<1	8.3

[a] See footnote *a* of Table II. [b] Assignments refer to the structure in Table II.

These spiro butenolides cannot be obtained by the direct addition of the di-Grignard reagents to the maleic anhydride.[2b] In many cases, the retro-Diels–Alder reaction was utilized for the synthesis of various unsaturated compounds.[10]

In a preliminary paper[11] we reported that spiro γ-lactones **21** and **22** produced by thermolysis the corresponding 1-oxaspiro[4.5]dec-3-en-2-one (**28**) and 1-oxaspiro[4.5]-dec-3-en-2-one (**30**).

With the object of developing the synthesis of spiro γ-butenolides, the pyrolysis of spiro lactones **14–17** was performed in toluene solution and in a scelled tube.[12] When comparing the results, it appears that the lactones **21** and **22** gave the cleanest and neatest products, by a simple distillation under vaccum.[13]

These possibilities are illustrated in Scheme V.

Furthermore, is appeared interesting to make a comparative and systematic study of the preceding lactones

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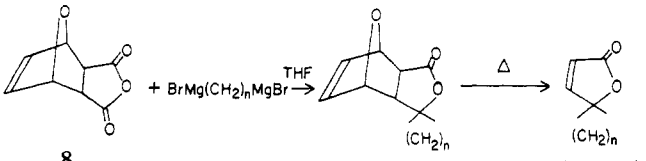
Scheme V



8 21, n = 4; 22, n = 5 29, n = 4; 30, n = 5

by ^{1}H and ^{13}C NMR. Our objective from the outset in employing all these different bicyclic systems was to demonstrate the chemioselectivity and regioselectivities of these spiroannelation processes, since we had a homogeneous series.

After an examination of the ^{1}H NMR spectra of all synthesized spiro γ-lactones (Tables II–IV) we found that the δ values are characteristic of the system studied (for 1′-H, 2′-H, 6′-H, 7′-H). These values do not vary whatever the spiranic ring may be, expect that 6′-H alone is affected.[14]

In fact, one observes in all the compounds (**11–24**) that there is shielding (cage effect), indicated by $\Delta\nu/J$ for 2′-H and 6′-H which increases from 2.0 to 2.5 in going from the five- to the six-membered spiro ring systems. For the same reason, one observes that 7′-H is more shielded than 1′-H, thus showing absence of symmetry (compared with the corresponding anhydrides) and the effect of the spiranic shielding nearby.

The $\Delta\nu/J$ values for the exo lactones are generally slightly higher, showing that the AX character of 1′-H and 7′-H is more pronounced for the endo than when they are for the exo compound. The δ values for 1′-H and 7′-H for the 7-oxa bicyclic system are completely changed because of the presence of oxygen.

The δ values for 2′-H and 6′-H reveal the stereochemistry of the product. For the endo lactones (these exo protons) they are more shielded than in the corresponding exo products, where the endo protons are influenced by the cage effect. Therefore, the stereochemistry can be determined solely by the chemical shifts.

Evidently, the coupling constants $J_{1',2'}$ and $J_{6',7'}$ render the stereochemical interpretation still easier (weak values for exo products). In general, the $J_{2',6'}$ is quite constant (7.5–9.5 Hz) and indicates that the angle between these hydrogens is small. Also, $J_{2',6'}$ does not vary from a spirocyclopentene to a spirocyclohexane compound; as the $\Delta\nu/J$ increases, we can conclude that the effect on 6′-H is created by the cyclohexane hydrogens.

The ^{1}H NMR data study of the endo lactones **13** and **14** introduces another stereochemical information. The lower $\Delta\nu/J$ values, when compared to all the other spiro lactones, are very likely to be due to the interaction existing between the *endo*-8′-H and the spirocycle hydrogens. This situation, particularly for compound **14**, generates a different conformation of the molecule, altering the dihedral angles.

Of course, very low $J_{1',2'}$ and $J_{6',7'}$ values for exo lactones **19**, **20**, **23**, and **24** indicate the absence of such interactions and dihedral angles of about 90°.

^{1}H NMR examination of the dispiro lactones confirms the proposed structures (**25–28**).

The trans lactones **25** and **27** present a 1′-H and 7′-H equivalence, as well as a 2′-H and 8′-H and a 6′-H and 12′-H equivalence, as indicated by J values and also by the integration.

In the case of the syn lactones (**26** and **28**), 2′-H and 12′-H are equivalent, as well as 6′-H and 8′-H, but 1′-H and 7′-H are magnetically nonequivalent, as depicted by the J values and especially by the integration.

Also, the $\Delta\nu/J$ values are characteristic of the size of the spiro ring (5.3 and 6.0 for cyclopentane, 7.3 and 8.7 for cyclohexane). It should be mentioned, however, that the difference between 7.3 and 8.7 can be explained by the straining closeness of the cyclohexane rings, present in the syn compound **28** and absent in the trans compound **26**. The hydrogens 6′-H and 8′-H become more shielded, increasing the $\Delta\nu$ contribution in the $\Delta\nu/J$ values.

The examination of ^{13}C NMR data reveals some general trends (Tables V and VI), as was previously reported.[15]

The spiro carbon chemical shifts are characteristic of the ring size (namely, 94–97 ppm for a cyclopentane spirannic carbon and 85–87 ppm for a cyclohexane spiranic carbon) and are found to be general.[2b,c] There is a difference of 7–10 ppm between the values of carbons α to the spiro ring, which is also characteristic of this unsymmetrical system. In fact, one of the two carbons is endo, i.e., in the concave part. It is interesting to note that changing n also changes δ on both carbons.

Another interesting point concerns the other carbon atoms (β, β′, γ) in the spiranic ring. In endo compounds, there is a certain change in δ for these carbons as we pass from an unsaturated system to a saturated system (**11** → **13**, **12** → **14**). This difference is smaller for the exo compounds (**17** → **19**, **18** → **20**, **21** → **23**, **22** → **24**). It confirms what has been already said in relation to the ^{1}H NMR, namely, that there is interaction between the *endo*-8′-H and the protons of the spiro ring in the endo spiro lactones.

This effect is even slightly felt on the 10′-C; i.e., in passing from n = 4 to n = 5 there is a greater difference in the endo (**11** → **12**, **13** → **14**; 0.4–0.5 ppm) than for the corresponding exo compounds (**17** → **18**, **19** → **20**; about 0.2 ppm). Since the spiro ring is endo in the first case, it even influences the methylene bridge.

The δ value of carbonyl is scarcely affected by the size of the spiro ring. The values are characteristic of lactones; however, the presence of an oxygen atom at the bridge position causes a slight shielding effect.

The 1- and 7-carbons become different when the spiro ring is six membered (for **21** and **23**, the difference between the two is 0.5 ppm; for **22** and **24** the difference is about 2 ppm) as in the case of oxygenated systems in position 10. One sees, therefore, the influence of spirocyclohexane on the 7′-carbon. Similarly, in the case of the bicyclo[2.2.2]oct-5-ene (**15** and **16**), the two carbons that form the ethylene bridge are nonequivalent, because of the absence of molecular symmetry caused by the spiro ring.

Experimental Section

Melting points were determined in capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. All boiling points are uncorrected. Analytical thin-layer chromatography was performed on EM silica gel 60 F 254 plates (0.25 mm). Column chromatography was carried out either on silica gel 60 F 254 (70–230-mesh ASTM) for dry column chromatography or on Woelm silica 32-63 for flash chromatography. Infrared spectra were obtained on a Beckman IR-12 spectrophotometer. ^{1}H NMR spectra were determined on a Bruker HX-90 spectrometer in $CDCl_3$ soln and are reported in δ units downfield from Me_4Si. ^{13}C NMR spectra were determined on a Bruker WP-80

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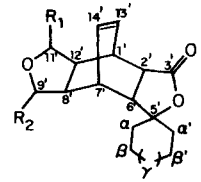
Table IV. ^{1}H NMR Comparative Data for Dispiro Lactones 25–28



compd	δ(hydrogen)[a] 1′-H	2′-H	6′-H	7′-H	8′-H	12′-H	coupling constants, Hz $J_{1',2'}$	$J_{2',6'}$	$J_{6',7'}$	Δν/J
25 (R_1 = $(CH_2)_4$, R_2 = O)	3.32	3.01	2.49	3.32	3.01	2.49	3.5 (=$J_{7',8'}$)	9 (=$J_{8',12'}$)	2.2 (=$J_{1',12'}$)	5.3
26 (R_1 = O, R_2 = $(CH_2)_4$)	3.59	3.08	2.45	2.97	2.45	3.08	3.5 (=$J_{1',12'}$)	9.5 (=$J_{8',12'}$)	2.2 (=$J_{7',8'}$)	6.0
27 (R_1 = $(CH_2)_5$, R_2 = O)	3.33	3.01	2.29	3.33	3.01	2.29	4 (=$J_{7',8'}$)	9 (=$J_{8',12'}$)	2 (=$J_{1',12'}$)	7.3
28 (R_1 = O, R_2 = $(CH_2)_5$)	3.61	3.08	2.16	2.91	2.16	3.08	4 (=$J_{1',12'}$)	9.5 (=$J_{8',12'}$)	2.5 (=$J_{7',8'}$)	8.7

[a] See footnote *a* of Table II.

Table V. ^{13}C NMR Chemical Shifts of Spiro Lactones 11–24

compd	δ(carbon)[a,e] 1′	2′[b]	3′	5′	6′[b]	7′	8′[c]	9′[c]	10′	11′	α	α′	β	β′	γ
11 (endo)	48.80	49.76	177.22	94.98	46.46	45.66	134.93	135.95	52.39		43.61	34.68	23.71	23.49	
12	48.73	50.85	177.44	85.76	45.22	44.93	134.71	136.10	52.90		41.41	33.15	23.05	22.54	25.46
13	40.24	53.34	178.17	93.88	48.22	40.24	26.05	23.20[d]	41.93		43.90	33.51	24.59	22.63[d]	
14	39.88	51.88	178.32	85.24	47.41	38.78	25.32	22.76[d]	42.29		40.24	32.05	23.12[d]	23.12[d]	26.27
15	31.98	47.27	178.02	96.88	46.46	31.98	133.02	133.32	25.17	22.83	42.44	34.68	23.12	22.83	
16	31.83	48.51	178.02	86.85	47.05	30.29	132.95	133.17	25.61	22.83[d]	40.76	33.51	22.54[d]	22.39	25.39
17 (exo)	49.68	46.68	177.15	95.19	45.61	49.68	137.71	138.95	44.19		42.66	33.44	22.98	22.68	
18	50.78	46.02	177.29	85.46	43.54	49.24	137.93	139.24	44.34		40.90	31.90	22.83	22.46	25.17
19	40.76	50.93	178.54	96.80	50.05	39.66	28.68	27.44	34.76		42.37	33.51	23.12	22.61	
20	40.10	50.93	178.46	86.93	50.49	37.54	28.83	27.29	34.98		40.39	32.12	22.98	22.54	25.17
21	82.10	49.83	174.95	95.05	48.73	81.59	136.83	137.63			42.00	34.46	22.90	22.68	
22	81.66	50.34	174.95	85.24	49.32	79.76	137.12	137.71			40.68	32.49	22.68	22.39	25.17
23	79.90	52.46	176.34	96.29	50.93	79.46	28.46	28.61			41.71	34.46	23.05	22.61	
24	79.54	52.54	176.34	86.56	52.02	77.56	28.61	28.61			40.24	32.71	22.83	22.46	25.24

[a] Chemical shifts are in δ (parts per million from Me_4Si). Solutions were 0.75 mol/L in $CDCl_3$. [b–d] Assignments could be interchanged. [e] See Table II for labeled structure.

Table VI. ^{13}C NMR Chemical Shifts of Dispiro Lactones 25–28

compd	δ(carbon)[a,e] 1′	2′	3′	5′	6′	7′	8′	9′	11′	12′	13′	14′	α	α′	β	β′	γ
25 (R_1 = $(CH_2)_4$, R_2 = O)	34.46	46.68[c]	176.41	96.51	44.78[c]	34.46	46.68[c]	176.41	96.51	44.78[c]	132.22	132.22	42.29 (+11α)	34.61 (11α′)	22.98 (11β)	22.76 (11β′)	
26 (R_1 = O, R_2 = $(CH_2)_4$)	34.90	46.54[c]	176.27	96.44	45.22[c]	34.39	45.22[c]	96.44	176.27	46.54[c]	132.37[b]	132.00[b]	42.80 (+9α)	34.90 (9α′)	23.12 (9β)	22.76 (9β′)	
27 (R_1 = $(CH_2)_5$, R_2 = O)	32.85	46.98[b]	176.41	86.78	46.76[b]	32.85	46.98[b]	176.41	86.78	46.76[b]	132.15	132.15	40.54 (+11α)	33.59 (11α′)	22.83 (11β)	22.32 (11β′)	25.24 (11γ)
28 (R_1 = O, R_2 = $(CH_2)_5$)	34.54	49.83[c]	176.19	86.56	45.07[c]	31.76	45.07[c]	86.56	176.19	49.83[c]	132.22[d]	132.22[d]	41.27 (+9α)	33.66 (9α′)	22.83 (9β)	22.24 (9β′)	25.32 (11γ)

[a] See footnote *a* of Table V. [b,c] Assignments could be interchanged. [d] Broadened peak, but not resolved. [e] See Table IV for labeled structure.

(20.1 M Hz) apparatus in $CDCl_3$ solution (0.75 mol/L) by using Me_4Si as an internal standard. Mass spectra were obtained in a Varian M-66 spectrometer, and microanalyses were performed by Chemalytics Inc.

Starting Materials. Magnesium turnings, 1,4-dibromobutane (1), 1,5-dibromopentane (2), *endo*-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (5), *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (8), bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic 2,3:5,6-dianhydride (10), maleic anhydride, and cyclopentadiene (as dicyclopentadiene) were commercially available.

Tetrahydrofuran was distilled from lithium aluminum hydride into oven-dried flasks and kept over sodium wire. Cyclopentadiene was obtained by distillation of dicyclopentadiene, prior to use, by the usual method.

***endo*-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Anhydride (3).** This anhydride was prepared according to Diels and Alder[4] from freshly distilled cyclopentadiene and maleic anhydride, and recrystallized as white needles from ligroin: mp 164–165 °C; 92% yield; ^1H NMR δ 1.68 (m, 2 H, ABX, J_{AB} = 9 Hz, J_{AX} = 1.5 Hz, 7-H), 3.49 (m, 2 H, 1-H and 4-H), 3.60 (m, 2 H, 2-H and 3-H), 6.26 (dd, 2 H, J = 1.7 Hz, 5-H and 6-H); IR ($CHCl_3$) 1875, 1845, 1780, 1230, 1085 cm^{-1}.

Isomerization of *endo*-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Anhydride. The exo adduct 6 was prepared according to the method of Craig[5] by heating the endo adduct 3 at 190 + 2 °C in an open flask immersed in an oil bath during 1.5 h. By successive recrystallization from benzene, the exo adduct 6 was obtained pure, and the mother liquors were heated an additional 0.5 h under the same conditions, for a 77% total yield. Recrystallization from benzene gave white crystals: mp 143 °C; ^1H NMR δ 1.57 (m, 2 H, ABX, J_{AX} = 1.5 Hz, J_{AB} = 10 Hz, 7-H), 3.00 (s, 2 H, 2-H and 3-H), 3.46 (m, 2 H, 1-H and 4-H), 6.31 (dd, 2 H, J = 2, 3.5 Hz, 5-H and 6-H); IR (CCl_4) 1875, 1840, 1780, 1210, 1070, 930, 890 cm^{-1}.

Preparation of Hydrogenated Dicarboxylic Anhydrides 4, 7, and 9. General Method. A mixture of the unsaturated anhydride (0.1 mol) and tetrahydrofuran (150 mL) was placed in a standard Parr bottle, along with 1.0 g of 5% palladium on charcoal catalyst, and the hydrogenation was carried out under an initial pressure at 0.1 bar (1.5 psi). After hydrogen uptake ceases, the catalyst was removed by filtration over Celite, using a tetrahydrofuran wash, the solvent was removed under reduced pressure, and the residue was recrystallized from benzene–ligroin.

***endo*-Bicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (4)**: white powder; mp 167 °C; 99% yield; ^1H NMR δ 1.27–1.90 (m, 6 H), 2.83 (m, 2 H, 1-H and 4-H), 3.40 (m, 2 H, 2-H and 3-H): IR ($CHCl_3$) 1855, 1820, 1775, 1225, 1075 cm^{-1}.

***exo*-Bicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (7)**: white crystals; mp 83.5–84 °C; 98% yield; ^1H NMR δ 1.28–1.91 (m, 6 H), 2.76–2.98 (m, 4 H, 1-H to 4-H); IR (CCl_4) 1875, 1835, 1780, 1230, 1085, 950, 910 cm^{-1}.

***exo*-7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (9)**: white powder; mp 113.5–114 °C; 94% yield; ^1H NMR δ 1.49–2.07 (m, 4 H, 5-H and 6-H), 3.17 (s, 2 H, 2-H and 3-H), 5.00 (dd, 2 H, J = 2.5, 3 Hz, 1-H and 4-H); IR ($CHCl_3$) 1880, 1850, 1780, 1235, 1090, 1010, 960 cm^{-1}.

Preparation of Spiro Lactones 11–24. General Method. The anhydride 3–9 (0.06 mol) in anhydrous THF (~50 mL) was added dropwise with stirring under nitrogen to 0.09 mol of the organodimagnesium compound prepared in the same solvent (150 mL). The reaction mixture was stirred for 2 h under an atmosphere of nitrogen. After hydrolysis with dilute (5–10%) HCl and stirring an additional hour at 40 °C, the organic layer was separated, the aqueous layer was extracted with ether, and the combined organic layers were dried over anhydrous sodium sulfate. The solution was concentrated in vacuo, and the residue was purified, either by distillation or crystallization.

2′,6′-*endo*-Spiro[cyclopentane-1,5′-[4]oxatricyclo-[5.2.1.$0^{2,6}$]dec-8′-en-3′-one] (11): recrystallized as white flakes from ether–ligroin; mp 74–75 °C; 85% yield; ^1H NMR δ 1.28–2.1 (m, 10 H), 2.87 (dd, 1 H, ABX, J_{AX} = 8.5 Hz, J_{AM} = 4.5 Hz, 6′-H), 3.07 (m, 1 H, 7′-H), 3.27 (m, 1 H, 1′-H), 3.39 (dd, 1 H, AM′X, J_{AX} = 8.5 Hz, $J_{M'X}$ = 4 Hz, 2′-H), 6.17 (m, 2 H, 8′-H and 9′-H); IR (CCl_4) 1770, 1660 cm^{-1}; mass spectrum, m/e (relative intensity) 204 (M^+, 100), 176 (59), 160 (31). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.41; H, 7.74.

2′,6′-*endo*-Spiro[cyclohexane-1,5′-[4]oxatricyclo-[5.2.1.$0^{2,6}$]dec-8′-en-3′-one] (12): recrystallized as white crystals from ether–ligroin; mp 48–49 °C; 75% yield; ^1H NMR δ 1.17–1.9 (m, 12 H), 2.71 (dd, 1 H, AMX, J_{AX} = 8.5 Hz, J_{AM} = 3.5 Hz, 6′-H), 3.04 (m, 1 H, 7′-H), 3.23 (m, 1 H, 1′-H), 3.41 (dd, 1 H, AM′X, J_{AX} = 8.5 Hz, $J_{M'X}$ = 5 Hz, 2′-H), 6.18 (m, 2 H, 8′-H and 9′-H); IR (CCl_4) 1765, 1640 cm^{-1}; mass spectrum, m/e (relative intensity) 218 (M^+, 100), 190 (66), 174 (44). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.85; H, 8.39.

2′,6′-*endo*-Spiro[cyclopentane-1,5′-[4]oxatricyclo-[5.2.1.$0^{2,6}$]decan-3′-one] (13): recrystallized as white flakes from ligroin; mp 47–48 °C; distillation bp 118–120 °C (0.02 mmHg); 84% yield; ^1H NMR δ 1.18–2.24 (m, 14 H), 2.42 (m, 1 H, 7′-H), 2.56 (dd, 1 H, AMX, J_{AX} = 10 Hz, J_AM = 4.5 Hz, 6′-H), 2.63 (m, 1 H, 1′-H), 3.10 (dd, 1 H, AM′X, J_AM = 10 Hz, $J_{M'X}$ = 6 Hz, 2′-H); IR (CCl_4) 1765 cm^{-1}; mass spectrum, m/e (relative intensity) 206 (M^+, 100), 178 (72), 162 (27). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.81: H, 8.88.

2′,6′-*endo*-Spiro[cyclohexane-1,5′-[4]oxatricyclo-[5.2.1.$0^{2,6}$]decan-3′-one] (14): distillation bp 122–124 °C (0.03 mmHg); 74% yield; ^1H NMR δ 1.17–2.04 (m, 16 H), 2.29–2.53 (m, 2 H, 6′-H and 7′-H), 2.62 (m, 1 H, 1′-H), 3.07 (dd, 1 H, AM′X, J_{AX} = 11 Hz, $J_{M'X}$ = 6 Hz, 2′-H); IR (neat) 1760 cm^{-1}; mass spectrum, m/e (relative intensity) 220 (M^+, 100), 192 (60), 176 (41). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.18; H, 9.22.

2′,6′-*endo*-Spiro[cyclopentane-1,5′-[4]oxatricyclo-[5.2.2.$0^{2,6}$]undec-8′-en-3′-one] (15): recrystallized as white plates from ether–pentane; mp 87–88 °C; 85% yield; ^1H NMR δ 1.14–1.65 (m, 4 H, 10′-H and 11′-H), 1.65–2.06 (m, 8 H), 2.44 (dd, 1 H, AMX, J_{AX} = 9.5 Hz, J_{AM} = 2 Hz, 6′-H), 2.76 (m, 1 H, 7′-H), 3.01 (dd, 1 H, AM′X, J_{AX} = 9.5 Hz, $J_{M'X}$ = 4 Hz, 2′-H), 3.07 (m, 1 H, 1′-H), 6.18 (m, 2 H, 8′-H and 9′-H); IR (CCl_4) 1770, 1670 cm^{-1}; mass spectrum, m/e (relative intensity) 218 (M^+, 100), 190 (52), 174 (33). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.88; H, 8.30.

2′,6′-*endo*-Spiro[cyclohexane-1,5′-[4]oxatricyclo-[5.2.2.$0^{2,6}$]undec-8′-en-3′-one] (16): recrystallized as white powder from ligroin; mp 72–73 °C; 75% yield; ^1H NMR δ 1.05–1.9 (m, 14 H), 2.21 (dd, 1 H, AMX, J_{AX} = 9 Hz, J_{AM} = 2 Hz, 6′-H), 2.72 (m, 1 H, 7′-H), 2.99 (dd, 1 H, AM′X, J_{AX} = 9 Hz, $J_{M'X}$ = 4 Hz, 2′-H), 3.05 (m, 1 H, 1′-H), 6.18 (m, 2 H, 8′-H and 9′-H); IR (CCl_4) 1765 cm^{-1}; mass spectrum, m/e (relative intensity) 232 (M^+, 100), 204 (62), 188 (37). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.40; H, 8.74.

2′,6′-*exo*-Spiro[cyclopentane-1,5′-[4]oxatricyclo-[5.2.1.$0^{2,6}$]dec-8′-en-3′-one] (17): distillation bp 104–105 °C (0.01 mmHg); 90% yield; ^1H NMR δ 1.48 (s, 2 H, 10′-H), 1.85 (m, 8 H), 2.26 (d, 1 H, AX, J_{AX} = 8 Hz, 6′-H), 2.79 (d, 1 H, AX, J_{AX} = 8 Hz, 2′-H), 3.01 (m, 1 H, 7′-H), 3.27 (m, 1 H, 1′-H), 6.22 (m, 2 H, 8′-H and 9′-H); IR (neat) 1765, 1245, 1170 cm^{-1}; mass spectrum, m/e (relative intensity) 204 (M^+, 100), 176 (42), 160 (31). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.32; H, 7.99.

2′,6′-*exo*-Spiro[cyclohexane-1,5′-[4]oxatricyclo[5.2.1.$0^{2,6}$]-dec-8′-en-3′-one] (18): recrystallized as white powder from heptane; mp 70–70.5 °C; 80% yield; ^1H NMR δ 1.47 (s, 2 H, 10′-H), 1.25–2.04 (m, 10 H), 2.07 (d, 1 H, AX, J_{AX} = 8 Hz, 6′-H), 2.79 (d, 1 H, AX, J_{AX} = 8 Hz, 2′-H), 3.0 (m, 1 H, 7′-H), 3.25 (m, 1 H, 1′-H), 6.22 (m, 2 H, 8′-H and 9′-H); IR (CCl_4) 1765 cm^{-1}; mass spectrum, m/e (relative intensity) 218 (M^+, 100), 190 (62), 174 (22). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31 Found: C, 76.88; H, 8.28.

2′,6′-*exo*-Spiro[cyclopentane-1,5′-[4]oxatricyclo-[5.2.1.$0^{2,6}$]decan-3′-one] (19): distillation bp 105–106 °C (0.01 mmHg); 90% yield; ^1H NMR δ 1.28 (m, 2 H, 10′-H), 1.05–2.06 (m, 12 H), 2.16 (d, 1 H, AX, J_{AX} = 8 Hz, 6′-H), 2.42 (m, 1 H, 7′-H), 2.66 (m, 1 H, 1′-H), 2.71 (d, 1 H, AX, J_{AX} = 8 Hz, 2′-H); IR (neat) 1765, 1240 cm^{-1}; mass spectrum, m/e (relative intensity) 206 (M^+, 100), 178 (72), 161 (35). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.50; H, 8.88.

2′,6′-*exo*-Spiro[cyclohexane-1,5′-[4]oxatricyclo[5.2.1.$0^{2,6}$]-decan-3′-one] (20): distillation bp 110–112 °C (0.01 mmHg); 80% yield; ^1H NMR δ 1.25 (s, 2 H, 10′-H), 1.02–1.83 (m, 14 H), 1.94 (d, 1 H, AX, J_{AX} = 9 Hz, 6′-H), 2.43 (m, 1 H, 7′-H), 2.61 (m, 1 H, 1′-H), 2.70 (d, 1 H, AX, J_{AX} = 9 Hz, 2′-H); IR (neat) 1770, 1220

cm^{-1}; mass spectrum, m/e (relative intensity) 220 (M^+, 100), 192 (47), 175 (32). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.22; H, 9.29.

2′,6′-*exo*-Spiro[cyclopentane-1,5′-[4,10]dioxatricyclo-[5.2.1.0^{2,6}]dec-8′-en-3′-one] (21): recrystallized as white crystals from ether–ligroin; mp 81–81.5 °C; 85% yield; ^1H NMR δ 1.5–2.26 (m, 8 H), 2.43 (d, 1 H, AX, J_{AX} = 7.5 Hz, 6′-H), 2.96 (d, 1 H, AX, J_{AX} = 7.5 Hz, 2′-H), 5.12 (s, 1 H, 7′-H), 5.27 (s, 1 H, 1′-H), 6.42 (s, 2 H, 8′-H and 9′-H); IR (CCl_4) 1770 cm^{-1}; mass spectrum, m/e (relative intensity) 206 (M^+, 100), 178 (74), 162 (35). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.69; H, 6.81.

2′,6′-*exo*-Spiro[cyclohexane-1,5′-[4,10]dioxatricyclo-[5.2.1.0^{2,6}]dec-8′-en-3′-one] (22): recrystallized as white powder from ether–ligroin; mp 94–95 °C; 75% yield; ^1H NMR δ 1.17–2.1 (m, 10 H), 2.21 (d, 1 H, AX, J_{AX} = 7.5 Hz, 6′-H), 2.92 (d, 1 H, AX, J_{AX} = 7.5 Hz, 2′-H), 5.14 (s, 1 H, 7′-H), 5.23 (s, 1 H, 1′-H), 6.41 (m, 2 H, 8′-H and 9′-H); IR (CCl_4) 1765 cm^{-1}; mass spectrum, m/e 220 (M^+, 100), 192 (52), 176 (31). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.68; H, 7.30.

2′,6′-*exo*-Spiro[cyclopentane-1,5′-[4,10]dioxatricyclo-[5.2.1.0^{2,6}]decan-3′-one] (23): recrystallized as white needles from ether–ligroin; mp 70–71 °C; 88% yield; ^1H NMR δ 1.3–1.63 (m, 2 H, 8′-H and 9′-H), 1.63–2.18 (m, 10 H), 2.42 (d, 1 H, AX, J_{AX} = 8 Hz, 6′-H), 2.96 (d, 1 H, AX, J_{AX} = 8 Hz, 2′-H), 4.72 (m, 1 H, 7′-H) 4.82 (m, 1 H, 1′-H); IR (CCl_4) 1770 cm^{-1}; mass spectrum, m/e (relative intensity) 208 (M^+, 89), 180 (100), 164 (43). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 69.08; H, 7.79.

2′,6′-*exo*-Spiro[cyclohexane-1,5′-[4,10]dioxatricyclo-[5.2.1.0^{2,6}]decan-3′-one] (24): crystallized as white powder from ether–ligroin; mp 104–105 °C; 78% yield; ^1H NMR δ 1.09–2.1 (m, 14 H), 2.21 (d, 1 H, AX, J_{AX} = 8 Hz, 6′-H), 2.95 (d, 1 H, AX, J_{AX} = 8 Hz, 2′-H), 4.77 (m, 1 H, 7′-H), 4.82 (m, 1 H, 1′-H); IR (CCl_4) 1770 cm^{-1}; mass spectrum, m/e (relative intensity) 222 (M^+, 81), 194 (100), 178 (29). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.22; H, 8.31.

Addition of Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic 2,3:5,6-Dianhydride (10) to (Butane-1,4-diyl)dimagnesium Dibromide (1). The same reaction conditions are employed for this Grignard reaction, except that 0.03 mol of dianhydride **10** was used, in the same solvent. Once the crude product was obtained after the usual workup as a white powder, the two isomers were separated by column chromatography.

2′,6′:8′,12′-*exo*,*exo*-Dispiro[cyclopentane-1,5′-[4,10]dioxatetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradec-13′-ene-3′,9′-dione-11′,1″-cyclopentane] (25) and 2′,6′:8′,12′-*exo*,*exo*-Dispiro[cyclopentane-1,5′-[4,10]dioxatetracyclo[5.5.2.0^{2,6,8,12}]tetradec-13′-ene-3′,11′-dione-9′,1″-cyclopentane] (26). The isomers were separated by flash chromatography[16] with ethyl acetate–benzene (15%) as the eluant. Recrystallization of each isomer from ethyl acetate–ligroin gave the following: white powder; mp (**25**) 170–170.5 °C; white flakes, mp (**26**) 182–182.5 °C; 86% yield obtained as mixture of isomers in a 65:35 ratio. Spectral characteristics of **25** are as follows: ^1H NMR δ 1.49–2.04 (m, 16 H), 2.49 (dd, 2 H, AMX, J_{AX} = 9 Hz, J_{AM} = 2.2 Hz, 6′-H and 12′-H), 3.01 (dd, 2 H, AM′X, J_{AX} = 9 Hz, $J_{M'X}$ = 3.5 Hz, 2′-H and 8′-H), 3.32 (m, 2 H, 1′-H and 7′-H), 6.20 (m, 2 H, 13′-H and 14′-H); IR (CCl_4) 1770, 1245 cm^{-1}; mass spectrum, m/e (relative intensity) 328 (M^+, 74), 299 (100), 286 (12), 60 (60). Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 73.04; H, 7.46. Spectral characteristics of **26** are as follows: ^1H NMR δ 1.49–2.04 (m, 16 H), 2.45 (dd, 2 H, AMX, J_{AX} = 9.5 Hz, J_AM = 2.2 Hz, 6′-H and 8′-H), 2.97 (m, 1 H, 7′-H), 3.08 (dd, 2 H, AM′X, J_{AX} = 9.5 Hz, $J_{M'X}$ = 3.5 Hz, 2′-H and 12′-H), 3.59 (m, 1 H, 1′-H), 6.18 (m, 2 H, 13′-H and 14′-H); IR (CCl_4) 1775, 1245 cm^{-1}; mass spectrum, m/e (relative intensity) 328 (M^+, 87), 299 (100), 286 (18), 60 (46). Anal. Found for $C_{20}H_{24}O_4$: C, 72.97; H, 7.31.

Addition of Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic 2,3:5,6-Dianhydride (10) to (Pentane-1,5-diyl)dimagnesium Dibromide (2). The same reaction conditions are employed for this Grignard reaction as for the synthesis of spiro lactones **25** and **26** above.

2′,6′:8′,12′-*exo*,*exo*-Dispiro[cyclohexane-1,5′-[4,10]dioxatetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradec-13′-ene-3′,9′-dione-11′,1″-cyclohexane] (27) and 2′,6′:8′,12′-*exo*,*exo*-Dispiro[cyclohexane-1,5′-[4,10]dioxatetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradec-13′-ene-3′,11′-dione-9′,1″-cyclohexane] (28). The isomers were separated by flash chromatography with ethyl acetate–benzene (15%) as the eluant. Recrystallization from ethyl acetate–ligroin gave the following: white flakes, mp (**27**) 285 °C dec; white powder, mp (**28**) 276–278 °C dec; 68% yield obtained as mixture of isomers in a 68:32 ratio. Spectral characteristics of **27** are as follows: ^1H NMR δ 1.28–1.89 (m, 20 H), 2.29 (dd, 2 H, AMX, J_{AX} = 9 Hz, J_{AM} = 2 Hz, 6′-H and 12′-H), 3.01 (dd, 2 H, AM′X, J_{AM} = 9 Hz, $J_{M'X}$ = 4 Hz, 2′-H and 8′-H), 3.33 (m, 2 H, 1′H and 7′-H), 6.24 (m, 2 H, 13′-H and 14′-H); IR (KBr) 1735, 1220 cm^{-1}; mass spectrum, m/e (relative intensity) 356 (M^+, 77), 327 (100), 314 (20). Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: 73.99; H, 7.89. Spectral characteristics of **28** are as follows: ^1H NMR δ 1.22–1.90 (m, 20 H), 2.16 (dd, 2 H, AMX, J_{AX} = 9.5 Hz, J_{AM} = 2.5 Hz, 6′-H and 8′-H), 2.91 (m, 1 H, 7′-H), 3.08 (dd, 2 H, AM′X, J_{AX} = 9.5 Hz, $J_{M'X}$ = 4 Hz, 2′-H and 12′-H), 3.61 (m, 1 H, 1′-H), 6.20 (m, 2 H, 13′-H and 14′-H); IR (KBr) 1735, ($CHCl_3$) 1745 cm^{-1}; mass spectrum, m/e (relative intensity) 356 (M^+, 68), 327 (100), 314 (27). Anal. Found for $C_{22}H_{28}O_4$: C, 73.95; H, 8.01.

Preparation of Spirocycloalkane 2-Butenolides 29 and 30. Synthesis of 1-Oxaspiro[4.4]non-3-en-2-one (29). The butenolide **29** was obtained by simple vacuum distillation of 5 mmol (1.03 g) of the spiro lactone **21**. Furan was evolved at a temperature of about 130 °C, and the remaining butenolide was collected by distillation: bp 116 °C (7 mmHg); 675 mg (98% yield); ^1H NMR δ 1.84 (m, 8 H), 5.80 (d, 1 H, AX, J_{AX} = 5.5 Hz, 3-H), 7.24 (d, 1 H, AX, J_{AX} = 5.5 Hz, 4-H); IR (CCl_4) 1772 cm^{-1}; mass spectrum, m/e (relative intensity) 138 (M^+, 100). Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.67; H, 7.39.

1-Oxaspiro[4.5]dec-3-en-2-one (30). This lactone was obtained as described for the above compound, from 5 mmol (1.10 g) of the spiro lactone **22**. Furan was evolved at ~130 °C, and the product was distilled: bp 124 °C (7 mmHg), 740 mg (97% yield); ^1H NMR δ 1.61 (m, 10 H), 5.80 (d, 1 H, AX, J_{AX} = 5.5 Hz, 3-H), 7.31 (d, 1 H, AX, J_{AX} = 5.5 Hz, 4-H); IR (CCl_4) 1776 cm^{-1}; mass spectrum, m/e (relative intensity) 152 (M^+, 100). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.88; H, 8.03.

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