of chloroform, and the combined organic layers were washed with 25 mL of brine, dried (Na_2SO_4), and concentrated in vacuo. The crude hydrazone obtained above was dissolved in 2 mL of methyl iodide and refluxed under N_2 for 3–5 h. The mixture was concentrated in vacuo and suspended in 25 mL of ether, which was treated with 12 mL of 1 N HCl. The two-phase mixture was rapidly stirred for 1–2 h and separated. The aqueous layer was extracted with 3 × 25 mL of methylene chloride, and the combined organics were washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated in vacuo to afford crude material, which was purified as appropriate.

Acknowledgment. We are grateful to the National Science Foundation for generous financial support of this work. A NIH-NSRA Fellowship (to PDE) is also gratefully acknowledged.

Manganese(III)-Mediated Spirodilactonization

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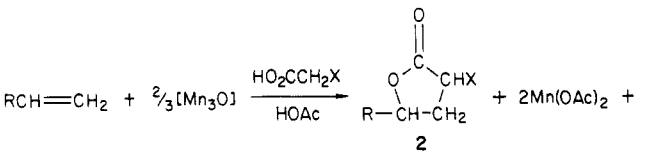
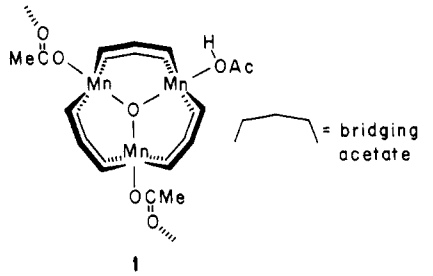
Manganese(III) oxidation of malonic acid in the presence of alkenes results in the formation of spiro-fused lactones, 2,7-dioxaspiro[4.4]nonane-1,6-diones. Terminal alkenes produce a mixture of the three possible diastereomers. The stereochemistry of the diastereomeric spirodilactones was determined by NMR and corroborated by the intensity of the coupled IR carbonyl stretching frequencies. 1,1,6,6-Tetrasubstituted 1,5-hexadienes give in one step tricyclic dilactones. Mechanistic and synthetic aspects of this reaction are discussed.

Manganese(III) acetate, **1**, oxidation of acetate ion in the presence of alkenes is known to produce lactones with high efficiency according to eq 1, X = H.[1-3] This reaction was



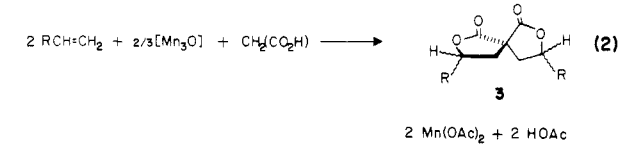


particularly intriguing to us because of its requirement of a trinuclear manganese oxidant to effect on overall two-electron oxidation of the organic moieties. In addition, the reaction is synthetically very useful, and we wished to expand on this synthetic utility.

Manganese(III) acetate is an easily prepared,[4] stable cinnamon brown solid when prepared as the hydrate. When manganese(III) was reduced to manganese(II) during a lactonization, the solution changed from dark brown to colorless. Thus, the course of all the present oxidations with manganese(III) were easily followed by inspection.

While investigating the mechanism of this lactonization reaction, we found that rapid ligand exchange occurred with the solvent which allowed substituted acetic acids to become incorporated into the manganese triangle.[5] Electron-withdrawing substituents on the acetic acid ligand greatly enhanced the reactivity of these ligands, allowing selective oxidation of these substituted ligands to take place. The rate of manganese(III) reduction was found to increase in the following order: acetic < chloroacetic < malonic < cyanoacetic acid by factors 1.3×10^1, 1.4×10^4, and 4.0×10^5, respectively at 120 °C.[1] In particular, cyanoacetic acid and 1-octene gave the α-cyanolactone, **2**, X = CN, R = *n*-hexyl, which crystallized out of the crude reaction workup in 69% yield. This prompted us to oxidize malonic acid in the anticipation of producing **2**, X = COOH, which should be capable of further functionalization or decarboxylation to the parent lactone **2**, X = H.

The lactone **2**, X = COOH, was indeed formed when 1 molar equiv of malonic acid was added to the lactonization mixture; however, it further reacted to yield the spirodilactone **3**, R = *n*-hexyl, in quantitative yield, eq 2. Thus,



(2)

the intermediate carboxy lactone **2**, X = COOH, proved more reactive to manganese(III) oxidation than malonic acid itself. This unusually facile spirodilactonization is the subject to this report.[6,7] During the final stages of this

(1) Fristad, W. E.; Peterson, J. R. *J. Org. Chem.* **1985**, *50*, 10.
(2) Heiba, E. I., Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 5905–5906.
(3) Bush, J. B., Jr.; Finkbeiner, H. *J. Am. Chem. Soc.* **1968**, *90*, 5903–5905.
(4) For numerous modifications of O. T. Christensen's procedure (*Z. Anorg. Allg. Chem.* **1901**, *27*, 321–328), see: Andrulis, P. J.; Dewar, M. J. S.; Dietz, R.; Hunt, R. L. *J. Am. Chem. Soc.* **1970**, *72*, 5473–5478. Finkbeiner, H. L.; Bush, J. B., Jr. Ger. Pat. 1 933 682; *Chem. Abstr.* **1970**, *72*, 89803*w*. Gilmore, J. R.; Mellor, J. M. *J. Chem. Soc. C* **1971**, 2355–2357. Heiba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 138–145.
(5) Peterson, J. R.; Hershberger, S. S., unpublished results.
(6) Spirodilactones of similar constitution have been previously made via ionic cyclization [(a) Leuchs, H.; Gieseler, E. *Chem. Ber.* **1912**, *45*, 2114–2129. (b) Fittig, R.; Hjelt, E. *Liebigs Ann. Chem.* **1882**, *216*, 64–67. (c) Ishido, Y.; Tsutsami, H.; Inaba, S. *J. Chem. Soc., Perkin Trans. 1* **1977**, 521–530. (d) Jaeger, V.; Guenther, H. J. *Tetrahedron Lett.* **1977**, 2543–2546], radical initiated cyclization [(e) Freidlina, R. Kh.; Velichko, F. K. *Synthesis* **1977**, 145–154. (f) Vinogradov, L. N.; Velichko, F. K.; Amriev, R. A.; Freidlina, R. Kh. *Izv. Acad. Nauk SSSR, Ser. Khim.* **1980**, 203–207], and in stepwise fashion [(g) Wagner, E.; Bobranski, B. *Pol. J. Pharmacol. Pharm.* **1977**, *29*, 565–569. (h) Vinogradov, M. G.; Fedorova, T. M.; Nikishin, G. I. USSR Pat. 461 925; *Chem. Abstr.* **1975**, *83*, 28127. Karapetyan, Z. T.; Dangyan, M. T. *Arm. Khim. Zh.* **1979**, *32*, 564–568].

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Table I. Spirodilactonization Results

entry	alkene	spirodilactone	spirodilactone yield,[a] %	diastereomer ratio,[b] ss:u:sa
1	1-hexene	4	100	9:47:44
2	1-octene	5	100	11:59:30
3	3,3-dimethyl-1-butene	6	42	2:48:50
4	α-methylstyrene	7	81	20:49:31
5	allyl chloride	8	30	9:60:31
6	1,1-diphenylethylene	9	93	
7	isobutene	10	51	
8	ethylene	11	29	
9	methylenecyclohexane	12	42	
10	cyclohexene	13	16	c
11	cyclopentene	14	40	0:92:8
12	1,1,6,6-tetraphenyl-1,5-hexadiene	15	12	
13	2,7-dimethyl-2,6-octadiene	16	40	

[a] Yields refer to chromatographed or recrystallized material. [b] Three diastereomers are possible: symmetrical-syn (ss); unsymmetrical (u); symmetrical-anti (sa). The designators refer to the relative orientation of highest priority lactone substituents, see Figure 1. [c] The six possible diastereomers were not separated.

work, a communication from Ito, Mishino, and Kurasawa reported their findings with the same manganese/malonic acid system.[8]

Results

The spirodilactonization was best accomplished by heating a stoichiometric solution of manganese(III) acetate, alkene, and malonic acid (0.67:2:1 mol, respectively) to 70 °C in glacial acetic acid. The dark mixture turned colorless within 2 h. A variety of alkenes were tested and are included in Table I. The gaseous alkenes (ethylene, isobutylene) were reacted under a pressure of 1 atm of the alkene. The yields of the unhindered terminal alkenes (entries 1 and 2) were essentially quantitative. 1,1-Disubstituted alkenes (entries 4, 6, 7, and 9) were quite satisfactory also. Allyl chloride (entry 5) was not particularly stable to the reaction conditions and resulted in a lower (30%) yield. Allyl bromide and allyl acetate failed to produce spirodilactones under these conditions. Cyclohexene (entry 10) was representative of most 1,2-disubstituted alkenes, and it produced only a low yield of spirodilactone. This was not surprising, as models show that any non-hydrogen substituents on carbons 4 and 9 of the spirodilactones generate very unfavorable steric interactions. Cyclopentene (entry 11) reacted much more effectively, since the two internal methylene units of the cyclopentane rings are pulled back further because of the smaller ring size.

The regiochemistry of lactonization was always correctly predicted by the mechanism proposed for the simple lactonization reaction.[1] This general mechanism as modified for spirodilactonization is shown in Scheme I. The stereochemical course of the reaction was not so clean. Diastereomers were formed in entries 1–5, 10, and 11. In all these cases, except 10, the three possible diastereomers were separated by crystallization or medium pressure chromatography. The relative orientation of the substituents on the spiro-fused lactone rings is defined as symmetrical-syn (s-s), unsymmetrical (u), and symmetrical-anti (s-a) in Figure 1.[9] In all cases the unsymmetrical diastereomer predominated followed by the symmetrical-anti. Models show very little specific interaction between substituents on C-3 and C-8 of the spiro system which accounted for the low stereoselectivity of the spirocyclization process. This contrasted with the often high stereoselectivity found in lactone annulation with acetic acid and 1,2-disubstituted alkenes.[1] The assignment of stereochemistry in these spirodilactones is discussed below.

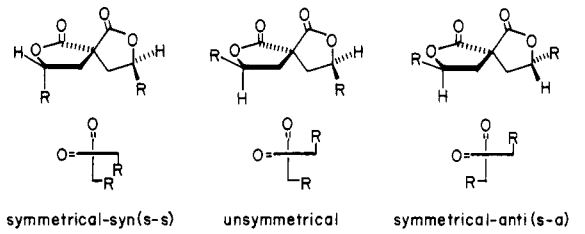
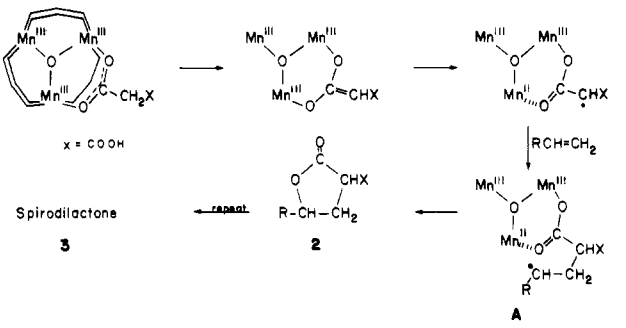
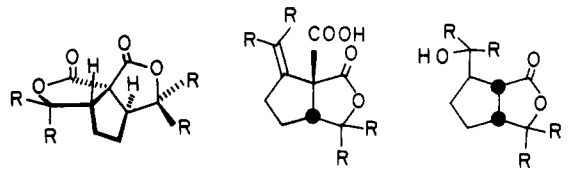


Figure 1. Spirodilactone diastereomer representations.

Scheme I



The final two entries of Table I illustrated the potential of 1,5-dienes to enter into the spirodilactonization. In each case a single tricyclic bridged spirodilactone was produced. While the stereochemistry was not rigorously proven, the cyclopenta[*a*]pentalene parent skeleton can accommodate only one stereoisomer of reasonable stability, and the cyclized compounds must be dilactones **15** and **16**. The C_2 axis of symmetry in **15** and **16** was easily deduced from their 13- and 7-line ^{13}C NMR spectra, respectively. The diene reactions were not as clean as all the previous cases, and two other monolactone products, **17** and **18**, were obtained in each case. The monolactone products were especially predominant with 1,1,6,6-tetraphenyl-1,5-hexadiene, **17a** and **18a** were formed in 42% and 23% yields, respectively. In this instance, closure of the second lactone ring required correct stereochemical formation of the C5–C9 bond as well as C–O bond formation to a doubly benzylic radical. This combination of effects allowed single electron transfer oxidation to give the very stabilized carbonium ion and subsequent formation of the alkene or the alcohol with concomitant decarboxylation. 2,7-Dimethyl-2,6-octadiene also gave the corresponding monolactone products **17b** and **18b**, however, in greatly reduced



15 R = Ph
16 R = Me
17 a R = Ph
b R = Me
18 a R = Ph
b R = Me

(7) Fristad, W. E.; Peterson, J. P.; Hershberger, S. S., presented at the 17th Great Lakes Regional Meeting of the American Chemical Society, June 1983.

(8) Ito, N.; Nishino, H.; Kurasawa, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3527–3528.

(9) Previous preparations of spirodilactones have either not commented on diastereomer separation or incorrectly stated that only two possibilities occur, see: Damin, B.; Forestiere, A.; Garapon, J.; Sillion, B. *J. Org. Chem.* **1981**, *46*, 3552–3554.

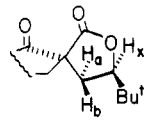
yield (8%, 8%). Thus, tertiary radicals underwent cyclization to give the lactone ring in reasonable yield, whereas doubly benzylic radicals apparently were too stable or hindered to cyclize the second lactone ring.

Discussion

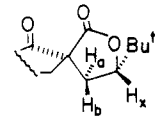
Formation. The formation of only spirodilactones **3** when the reaction was carried out with exactly the stoichiometric ratio of manganese(III): malonic acid:alkene was at first unexpected. Even a tenfold excess of malonic acid, however, still gave a quantitative yield (based on oxidant or olefin) of spirodilactones from 1-hexene. None of the presumed intermediate carboxy lactone **2**, X = COOH, could be isolated. On the other hand, the carboxymethyl lactone **2**, X = CO_2Me, could be prepared in reasonable yield 76%) from monomethyl malonate for identification. The use of monomethyl malonate appeared to be general and a very acceptable route into carboxymethyl lactones. Conditions for this reaction were identical with the spirodilactone procedure; however, a slight excess of monomethyl malonate was used to minimize overoxidation of **2**, X = CO_2Me. This relative inertness of **2**, X = CO_2Me, to further oxidation indicates the tremendous importance of a free carboxylic acid to effect the rapid second oxidation and lactonization of the intermediate **2**. This free carboxylic acid moiety is presumably required for complexation to the Mn(III) to effect enolization and further oxidation.

Relatively little synthetic optimization was conducted because of the early quantitative yields which were obtained. We have observed that higher temperatures (refluxing acetic acid) led to lower yields of spirodilactones (e.g., 55% from 1-octene). The reaction conditions of Kurasawa et al. involved refluxing acetic acid, and their yields are uniformally lower than ours at 70 °C by 15–80%.[8] There was no benefit in lowering the temperature further, as hydrated manganese(III) acetate had low solubility at 50–60 °C. Increasing the amount of oxidant to 33% above the stoichiometric amount resulted in a decreased yield (70%) and so was not further investigated.

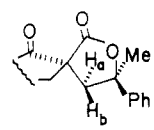
Stereochemistry. Assignment of the relative stereochemistry to the diastereomers produced in the spirodilactonization was on the basis of careful analysis of the ^1H NMR spectra. Identification of the unsymmetrical diastereomer was always trivial because the lack of symmetry left all the lactone ring hydrogens distinctly visible in the ^1H NMR spectrum. In the two symmetrical diastereomers the C_2 axis of symmetry reduced the number of hydrogen resonances by one-half. All the diastereomer sets from entries 1–5 and 11 in Table I behaved in the same fashion, and so only the assignments for **6s–s** and **6s–a** will be



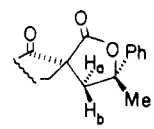
6 s-s



6 s-a



7 s-s



7 s-a

described. Entry 4, α-methylstyrene, proved more difficult and will be treated separately. Table II lists the chemical shifts and coupling constants for **6s-s** and **6s-a**. The deshielding (vida supra) of protons syn to the adjacent lactone ring carbonyl was due to the rather rigid ring system which held these protons in the deshielding cone of this carbonyl.[10] Thus, the isomer with the larger H_x chemical shift must be **6s-s**. This assignment is also consistent with the larger chemical shift of H_a and smaller coupling constants of cis H_a–H_x in **6s-s**.[11]

Table II. ^1H NMR Analysis of 6ss and 6sa

compound	hydrogen	δ	J, Hz
6s-s	H_x	4.67	6.2, 10.2
	H_a	2.58	6.2, 13.1
	H_b	2.02	10.2, 13.1
6s-a	H_x	4.20	6.1, 10.5
	H_a	2.46	10.5, 13.0
	H_b	2.24	6.1, 13.0
7s-s	H_a	2.70	13.3
	H_b	2.15	13.3
7s-a	H_a	3.20	13.3
	H_b	2.65	13.3

The stereochemical assignment for the products from α-methylstyrene, **7s-s** and **7s-a**, was less straightforward since there were no distinguishing protons on C-3 and C-8, and the anisotropic effect of the benzene rings could not be safely predicted. Difference NOE experiments indicated that the compound with H_a = 2.70 had a *syn*-methyl group (**7s-s**) and that H_b = 2.65 had a *syn*-methyl group (**7s-a**). This assignment left H_a in **7s-a** to be more deshielded than H_a in **7s-s**. This required that the phenyl group further deshield H_a in **7s-a** as was also observed in **9**. The identification of all the spirodilactone diastereomers was thus safely secured.

Additional stereochemical proof for all the spirodilactones came from a rather unexpected source. The infrared spectra of s-s/s-a pairs allowed complete and unambiguous prediction of stereochemistry with no NMR knowledge. Determination of stereochemistry at saturated carbon atoms by IR is not common; however, it has a firm theoretical basis in this case and seems worth noting.

The carbonyls of the spirodilactone skeleton acted as a coupled oscillator system, and therefore had IR-active symmetric and antisymmetric stretches. The antisymmetric absorption was at higher frequency.[12] The intensity of each absorption was dependent on the change in dipole moment within each stretching mode. Simple geometric addition of the dipole vectors of each carbonyl gave the magnitude of the resultant vector. When Dreiding models of the spirodilactones were placed in conformations which oriented the bulkiest R group in a pseudoequatorial position, the carbonyls were disposed at the dihedral angles shown in Figure 2. From models and simple vector addition the lower frequency symmetric stretch was assigned to the more intense s-s isomer, while the higher frequency antisymmetric stretch was attributed to the s-a isomer. This is exemplified by the carbonyl region of **6s-s** and **6s-a**. For **6s-a** the higher frequency (antisymmetric) stretch was the more intense absorption (2.27:1 transmission ratio) while **6s-s** gave a more intense lower frequency (symmetric) stretch (1.35:1 transmission ratio). This effect was consistently observed for every diastereomeric pair of spirodilactones synthesized. The observation and corrolation of coupled carbonyl oscillators has been noticed before, primarily in anhydrides;[12] however, this usage as

(10) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1981; p 189.
(11) Heathcock, C. H.; Young, S. D.; Hagen, J. P.; Pirrung, M. C.; White, C. J.; Van Derveer, D. *J. Org. Chem.* **1980**, *85*, 3846–3856. Bystrom, S.; Hogberg, H. E.; Norm, T. *Tetrahedron* **1981**, *37*, 2249–2254.
(12) Nyquist, R. A.; Kagel, R. O. "Infrared and Raman Spectroscopy, Part B", Brame, F. G., Grasseli, J. G., Ed.; Marcel Dekker: New York, 1977; pp 464–465.

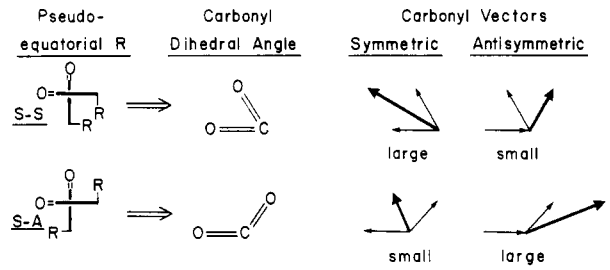
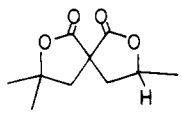


Figure 2. Stereochemistry by infrared; carbonyl vector addition which allows the prediction of the symmetric and antisymmetric carbonyl intensities.

a stereochemical proof appears to be unique.

Physical Properties. Spiro-fused compounds have long attracted the attention of chemists as synthetic targets and as models for specific physical properties. All the spirodilactones prepared here showed several interesting physical properties which were either a boon or a bane. Virtually all the compounds had exceptionally low solubility in typical organic chromatography solvents, despite their reasonable melting points (usually 100–200 °C), which made separation of larger quantities difficult. The ^{13}C and ^{1}H NMR spectra were simplified by the C_2 axis of symmetry in the two symmetrical diastereomers (s-s and s-a). Characteristically, lactone ring protons syn to the carbonyl of the neighboring lactone ring were deshielded by approximately 0.2–1.0 ppm, which allowed ready identification of each of the lactone methylene protons. A similar effect has been observed before in spiro[4.4]nonane-1,6-diones.[13,14] The infrared spectra of the spirodilactones were characterized by two carbonyl absorbances in the 1790–1750-cm^{-1} region. This was a result of the two carbonyls acting as a coupled oscillator system, which gave rise to both symmetric and antisymmetric absorptions. The appearance of these two absorptions in a chromatographic fraction indicated the spirodilactone system, and the relative intensities of each band allows assignment of the stereochemistry for compounds **4-8** (vide infra).

Applications of Spirodilactones. Spirodilactones have also been shown to possess useful properties as a polyester cross-linking agent,[15] and possible tranquilizers or sedatives.[16,17] Compounds as structurally simple as **3**, R = Me, have been shown to have tranquilizing activity in mice, rabbits, and cats.[18] It is interesting in this regard to note that spirodilactone **3**, R = Me, has been considered as a possible metabolite of the barbituate ipronal.[19] Metabolism studies in rats and dogs have also resulted in the isolation of spirodilactone **19** after administration of butalbital, **20**.[20] The present spirodilactonization method should represent a very simple and direct entry into many of these compounds for further metabolic and pharmaceutical studies.



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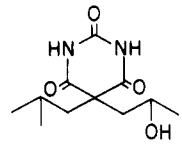

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Conclusion

Manganese(III) acetate mediated a very high yielding spirodilactonization of malonic acid and two alkenes in one step. All possible diastereomers were produced, separated, and characterized. Appropriately substituted 1,5-dienes were also utilized to assemble tricyclicdilactones. The mechanism appears to proceed through the usual manganese(III) lactonization process which allowed complete prediction of the regiochemical outcome. An interesting and unique infrared method of stereochemical identification was presented and found to be completely consistent through all six diastereomeric pairs.

Experimental Section

Melting points were determined with an Electrothermal apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a Varian HFT-80 (80 MHz) or a Nicolet 300-MHz instrument. Chemical shifts are reported in parts per million relative to internal $(CH_3)_4Si$ in $CDCl_3$ unless specified otherwise. Mass spectra were obtained with an AE1 Kratos MS-30 (electron impact) or a Finnigan 4000 (chemical ionization) spectrometer. Infrared spectra were obtained on a Beckman 4250 spectrophotometer. Gas chromatography was performed with a Varian Model 3700 gas chromatograph equipped with FID's and a Hewlett-Packard 3390A integrator. The columns used were 5% Carbowax 20M on 100/120-mesh Chromosorb W, 0.3 cm × 6 m; 10% SF-96 on 80/100-mesh Chromosorb W, 0.3 cm × 6 m; or silver nitrate/ethylene glycol on 80/100-mesh Chromosorb P to determine alkenes and volatile lactones. Products were isolated by medium pressure liquid chromatography (FMI pump, silica gel column, refractive index detector, Altex Model 156).

Starting alkenes were commercially obtained except for the dienes which were prepared by standard Grignard or Wittig techniques. Manganese(III) acetate was prepared by literature methods.[4]

Representative Spirodilactonization Reaction. In a typical reaction, manganese(III) acetate dihydrate[4] (2.70 g, 3.35 mmol $[Mn_3O]$ = 10 mmol Mn(III)) was weighed into a 50-mL flask equipped with a magnetic stirrer. Glacial acetic acid, 25 mL, was added and the flask placed in a 70 °C oil bath and stirred. The manganese(III) acetate did not all dissolve. Malonic acid (0.26 g, 2.5 mmol) was added, immediately followed by addition of 5 mmol of the appropriate olefin. The flask was fitted with a reflux condenser and gas inlet tube (N_2) and the reaction allowed to proceed until the reaction mixture turned colorless, usually in 2 h. (For reactions with low boiling olefins, 1-hexene, 3,3-dimethyl-1-butene, allyl chloride, cyclopentene, and cyclohexene, a 1–2-fold excess of the olefin was employed and a 25-mL flask was utilized. Ethylene and isobutylene involved use of a two-necked 50-mL flask, flushing the reaction with the appropriate gaseous olefin and fitting a balloon containing the olefin on the gas inlet tube.) Upon cooling, white–pale pink $Mn(OAc)_2$ usually precipitated. After cooling, the reaction mixture was quenched with 250 mL of water and extracted with 50–75 mL of dichloromethane or ether. (Dichloromethane was preferred as it dissolved the insoluble dilactones and dissolved less acetic acid than ether.) The organic extract was washed with saturated $NaHCO_3$ until the washings were no longer acidic, subsequently washed twice with water or saturated NaCl, dried ($MgSO_4$), and concentrated to give spirodilactones. MPLC separation of diastereomeric dilactones employed 20–40% ethyl acetate/hexane. Recrystallizations were accomplished with dichloromethane and hexane mixtures.

Structural Data for Compounds in Table I. (±)-(3α,5β,8R*)-3,8-Dibutyl-2,7-dioxaspiro[4.4]nonane-1,6-dione

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(4s-s): mp 120–120.5 °C (lit.[21] mp 117–118 °C); IR (KBr) 2960, 2925, 1768, 1753 (strongest C=O), 1350, 1190, 1165 cm^{-1}; ^1H NMR δ 5.1–4.6 (m, 2 H), 2.79 (dd, J = 6.2, 13 Hz, 2 H), 1.88 (dd, J = 9.4, 13 Hz, 2 H), 2.7–2.15 (m, 12 H), 0.92 (t, J = 6 Hz, 6 H).

(±)-(3α,5α,8*S)-3,8-Dibutyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (4u)**: mp 106–106.5 °C (lit.[21] mp 102.5–103 °C); IR (KBr) 2960, 2930, 1775, 1760–1746 (strongest C=O), 1465, 1355, 1210, 1178 cm^{-1}; ^1H NMR δ 4.95–4.60 (m, 1 H), 4.60–4.25 (m, 1 H), 2.78 (dd, J = 5.7, 12.9 Hz, 1 H), 2.64 (dd, J = 8.3, 13.2 Hz, 1 H), 2.18 (dd, J = 6.8, 13.2 Hz, 1 H) 1.89 (dd, J = 9.9, 12.9 Hz, 1 H), 1.60–1.20 (m, 12 H), 0.92 (t, J = 6.4 Hz, 6 H); MS exact mass calcd for $C_{15}H_{24}O_4$ m/z 268.1673, found 268.1815.

(±)-(3α,5α,8*R)-3,8-Dibutyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (4s-a)**: mp 100.5–101 °C; IR (KBr) 2960, 2925, 1774 (strongest C=O), 1750, 1460, 1345, 1210, 1195 cm^{-1}; ^1H NMR δ 4.65–4.25 (m, 2 H), 2.57 (dd, J = 7.9, 20 Hz, 2 H), 2.27 (dd, J = 7.9, 20 Hz, 2 H), 2.0–1.1 (m, 12 H), 0.92 (t, J = 6.2 Hz, 6 H).

(±)-(3α,5β,8*R)-3,8-Dihexyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (5s-s)**: mp 123–123.5 °C (lit.[8] mp 116.5–118 °C); IR (KBr) 2955, 2920, 1770, 1752 (strongest C=O), 1450, 1350, 1187, 1163 cm^{-1}; ^1H NMR δ 5.1 – 4.7 (m, 2 H), 2.83 (dd, J = 6, 14 Hz, 2 H), 1.93 (dd, J = 10, 14 Hz, 2 H), 1.6–1.2 (m, 20 H), 0.95 (t, J = 7 Hz, 6 H).

(±)-(3α,5α,8*S)-3,8-Dihexyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (5u)**: mp 112–112.5 °C (lit.[8] mp 110–111 °C); IR (KBr) 2960, 2925, 1775, 1762–1745 (strongest C=O), 1450, 1355, 1210, 1178 cm^{-1}; ^1H NMR δ 4.95–4.65 (m, 1 H), 4.65–4.25 (m, 1 H), 2.77 (d, J = 5.6, 12.7 Hz, 1 H), 2.63 (dd, J = 8.3, 13.0, 1 H), 2.24 (dd, J = 6.8, 13.0 Hz, 1 H), 1.90 (dd, J = 10.0, 12.7 Hz, 1 H), 1.65–1.1 (m, 20 H), 0.92 (t, J = 6.6 Hz, 6 H).

(±)-(3α,5α,8*R)-3,8-Dihexyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (5s-a)**: mp 112.5–113 °C (lit.[8] mp 112.5–113 °C); IR (KBr) 2960, 2925, 1775 (strongest C=O), 1750, 1460, 1345, 1210 cm^{-1}; ^1H NMR δ 4.7–4.2 (m, 2 H), 2.55 (dd, J = 7.4, 19 Hz, 2 H), 2.27 (dd, J = 7.4, 19 Hz, 2 H), 1.95–1.1 (m, 20 H), 0.92 (t, J = 6.3 Hz, 6 H); MS exact mass calcd for $C_{19}H_{32}O_4$ m/z 324.2302, found 324.2322.

(±)-(3α,5β,8*R)-3,8-Bis(2-methyl-2-propyl)-2,7-dioxaspiro[4.4]nonane-1,6-dione (6s-s)**: IR (KBr) 2960, 2925, 1775, 1758 (strongest C=O), 1460, 1395, 1370, 1345, 1192, 1157, 1065 cm^{-1}; ^1H NMR δ 4.67 (dd, J = 6.2, 10.2 Hz, 2 H), 2.58 (dd, J = 6.2, 13.1 Hz, 2 H), 2.02 (dd, J = 10.2, 13.0, 2 H), 0.97 (s, 18 H).

(±)-(3α,5α,8*S)-3,8-Bis(2-methyl-2-propyl)-2,7-dioxaspiro[4.4]nonane-1,6-dione (6u)**: mp 202.5–203 °C; IR (KBr) 2960, 2930, 1772 (strongest C=O), 1747, 1470, 1395, 1365, 1345, 1220, 1205, 1180 cm^{-1}; ^1H NMR δ 4.56 (dd, J = 5.8, 10.8 Hz, 1 H), 4.25 (dd, J = 6.1, 10.8 Hz, 1 H), 2.82 (dd, J = 10.8, 13.3 Hz, 1 H), 2.58 (dd, J = 5.8, 13.0 Hz, 1 H), 2.03 (dd, J = 6.1, 13.3 Hz, 1 H), 2.01 (dd, J = 10.8, 13.0 Hz, 1 H), 1.00 (s, 9 H), 0.97 (s, 9 H).

(±)-(3α,5α,8*R)-3,8-Bis(2-methyl-2-propyl)-2,7-dioxaspiro[4.4]nonane-1,6-dione (6s-a)**: mp 214–215 °C; IR (KBr) 2960, 2920, 1772 (strongest C=O) 1745, 1475, 1378, 1220, 1200, 1183, 1055 cm^{-1}; ^1H NMR δ 4.2 (dd, J = 6.1, 10.5 Hz, 2 H), 2.46 (dd, J = 10.5, 13.0 Hz, 2 H), 2.24 (dd, J = 6.1, 13.0 Hz, 2 H), 0.99, (s, 18 H); MS exact mass calcd for $C_{11}H_{16}O_4$ (m – 56 (isobutylene)/z 212.1049, found 212.1049.

(±)-(3α,5β,8*R)-3,8-Dimethyl-3,8-diphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (7s-s)**: mp 216.5–217 °C (lit.[8] mp 218–219 °C); IR (KBr) 3090, 3060, 3030, 2980, 2930, 1775, 1753 (strongest C=O), 1600, 1495, 1447, 1437, 1380, 1300, 1240, 1230, 1165, 1142, 1130, 1067, 1012, 950, 762, 700 cm^{-1}; ^1H NMR δ 7.5–7.2 (m, 10 H), 3.25 (d, J = 13.3 Hz, 2 H), 2.77 (d, J = 13.3 Hz, 2 H), 1.78 (s, 6 H).

(±)-(3α,5α,8*S)-3,8-Dimethyl-3,8-diphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (7u)**: mp 96.5–97 °C (lit.[8] mp 98.5–99.5 °C); IR (KBr) 3060, 3025, 3005, 2980, 1775, 1753 (strongest C=O), 1595, 1495, 1450, 1385, 1320, 1305, 1235, 1160, 1140, 1075, 1070, 1030, 1015, 995, 950, 915, 760, 695 cm^{-1}; ^1H NMR δ 7.5–7.1 (m, 10 H), 3.15 (d, J = 13.2 Hz, 1 H), 2.80 (d, J = 13.6 Hz, 1 H), 2.80 (d, J = 13.2 Hz, 1 H), 2.10 (d, J = 13.6 Hz, 1 H), 1.90 (s, 3 H), 1.65 (s, 3 H); MS exact mass calcd for $C_{21}H_{20}O_4$ m/z 336.1362, found 336.1371.

(±)-(3α,5α,8*R)-3,8-Dimethyl-3,8-diphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (7s-a)**: mp 141–143 °C (lit.[8] mp 162–163 °C); IR (KBr) 3070, 3030, 3010, 2990, 2940, 1778 (strongest C=O), 1754, 1600, 1495, 1445, 1383, 1315, 1300, 1240, 1230, 1205, 1142, 1065, 987, 957, 910, 770, 700 cm^{-1}; ^1H NMR δ 7.5–7.2 (m, 10 H), 2.67 (d, J = 13.3 Hz, 2 H), 2.17 (d, J = 13.3 Hz, 2 H), 1.75 (s, 6 H).

(±)-(3α,5β,8*R)-3,8-Bis(chloromethyl)-2,7-dioxaspiro[4.4]nonane-1,6-dione (8s-s)**: IR (KBr) 2950, 1775, 1768 (strongest C=O) 1450, 1440, 1425, 1370, 1340, 1275, 1205, 1190, 1160, 1150, 1035, 1020 cm^{-1}; ^1H NMR δ 5.1 (m, 2 H), 3.74 (d, J = 8 Hz, 4 H), 2.85 (dd, J = 6.5, 13.5 Hz, 2 H), 2.25 (dd, J = 9, 13.5 Hz, 2 H).

(±)-(3α,5α,8*S)-3,8-Bis(chloromethyl)-2,7-dioxaspiro[4.4]nonane-1,6-dione (8u)**: mp 95–96 °C; IR (KBr) 2970, 2920, 1775, 1755 (strongest C=O), 1450, 1430, 1412, 1375, 1347, 1340, 1226, 1210, 1195, 1170, 1147, 1066, 1023, 952 cm^{-1}; ^1H NMR δ 5.3–4.9 (m, 1 H), 4.9–4.5 (m, 1 H), 3.80 (d, J = 7.5 Hz, 2 H), 3.75 (d, J = 8.0 Hz, 2 H), 2.85 (dd, J = 7.5, 13 Hz, 2 H), 2.45 (dd, J = 8.0, 13 Hz, 2 H).

(±)-(3α,5α,8*R)-3,8-Bis(chloromethyl)-2,7-dioxaspiro[4.4]nonane-1,6-dione (8s-a)**: mp 135–136 °C; IR (KBr) 2965, 2920, 1770 (strongest C=O), 1755, 1437, 1370, 1340, 1295, 1225, 1192, 1175, 1135, 1080, 1050, 1030, 1005, 940 cm^{-1}; ^1H NMR δ 4.75 (m, 2 H), 3.85 (d, J = 6.7 Hz, 4 H), 2.82 (dd, J = 5.5, 14.0 Hz, 2 H), 2.48 (dd, J = 7.7, 14.0 Hz, 2 H); MS exact mass calcd for $C_9H_{10}O_4Cl_2$ (m + 1)/z 252.9957, found 252.9911; (m – 49 (CH_2Cl))/z 203.0111, found 202.9932.

3,3,8,8-Tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (9): mp 286–288 °C (lit.[8] mp 284.5–285 °C); IR (KBr) 3080, 3060, 3025, 2935, 1795 (strongest C=O), 1765, 1490, 1450, 1278, 1233, 1228, 1203, 1175, 1045, 1033, 985, 750, 705 cm^{-1}; ^1H NMR δ 7.39–7.20 (m, 20 H), 3.0 (d, J = 13.4 Hz, 2 H), 2.4 (d, J = 13.4 Hz, 2H); MS exact mass calcd for $C_{31}H_{24}O_4$ m/z 460.1675, found 460.1650.

3,3,8,8-Tetramethyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (10): mp 133–133.5 °C; IR (KBr) 2990, 2925, 1767, 1742 (strongest C=O), 1445, 1387, 1375, 1295, 1272, 1157, 1120, 1097, 1022, 975, 922 cm^{-1}; ^1H NMR δ 2.75 (d, J = 13.4 Hz, 2 Hz) 2.20 (d, J = 13.4 Hz, 2 H), 1.60 (s, 6 H), 1.46 (s, 6 H); MS exact mass calcd for $C_{11}H_{16}O_4$ m/z 212.1049, found 212.1049.

2,7-Dioxaspiro[4.4]-nonane-1,6-dione (11): mp 108–109 °C (lit.[6a] mp 109–110 °C), IR (KBr) 2980, 2920, 1772 (strongest C=O), 1750, 1485, 1452, 1445, 1375, 1232, 1225, 1205, 1175, 1023, 1015, 1003 cm^{-1}; ^1H NMR δ 4.65 (dt, J = 8.4, 16.3 Hz, 2 H), 4.47 (ddd, J = 4.1, 7.3, 16.3 Hz, 2 H), 2.81 (ddd, J = 4.1, 7.3, 13.1 Hz, 2 H), 2.34 (dt, J = 8.4, 13.1 Hz, 2 H).

16,19-Dioxatrispiro[5.1.1.5.2.2]nonadecane-17,18-dione (12): mp 166–166.5 °C lit.[8] mp 165–166 °C); IR (KBr) 2930, 1767 (strongest C=O), 1740, 1490, 1270, 1220, 1210, 960, 950 cm^{-1}; ^1H NMR δ 2.65 (d, J = 13.6 Hz, 2 H), 2.10 (d, J = 13.6 Hz, 2 H), 1.92–1.25 (m, 20 H); MS exact mass calcd for $C_{17}H_{24}O_4$ m/z 292.1675, found 292.1686.

Dodecahydro-3,3′-(2*H*,2*H*′)-spirobi[benzofuran]-2,2′-dione (13): mixture of isomers not separated; IR (thin film) 2940, 1790–1750 br, 1460, 1450, 1350, 1305, 1265, 1215–1205 br, 905, 730 cm^{-1}; ^1H NMR δ 4.8–3.7 (m, 2 H), 2.65–1.95 (m, 2 H), 1.95–0.90 (m, 16 H); MS exact mass calcd for $C_{15}H_{20}O_4$ m/z 264.1362, found 264.1365.

(3α,3aβ,6aβ,3′a*S,6′a*S**)-3,3′(2*H*,2*H*′)-Spirobi[cyclopenta[*b*]furan]-2,2′-dione (14u)**: mp 121–123 °C; IR (KBr) 2970, 2950, 1772, 1753–1742 (strongest C=O), 1447, 1352, 1187, 1146, 1105, 975, 936, 906 cm^{-1}; ^1H NMR δ 5.17 (dt, J = 2.35, 5.48, 1 H), 4.95 (dt, J = 3.16, 5.98 Hz, 1 H), 2.83 (m, 2 H), 2.20–1.80 (m, 8 H), 1.80–1.50 (m, 4 H).

(3α,3aβ,6aβ,3′a*R,6′a*R**)-3,3′(2*H*,2*H*′)-Spirobi[cyclopenta[*b*]furan]-2,2′-dione (14s-a)**: mp 166–167 °C; IR (KBr) 2987, 2950, 2880, 1772, 1750 (strongest C=O), 1450, 1350, 1323, 1190, 1145, 985, 907 cm^{-1}; ^1H NMR δ 5.02 (dt, J = 1.2, 5.0 Hz, 2 H), 2.35 (m, 2 H), 2.1–1.8 (m, 8 H), 1.8–1.5 (m, 4 H); MS exact mass calcd for $C_{13}H_{16}O_4$ m/z 236.1049, found 236.1057.

Reactions of 1,1,6,6-tetraphenyl-1,5-hexadiene were worked up with the following changes. After washing with aqueous $NaHCO_3$, the lactone acids formed an insoluble suspension in dichloromethane. The lactone acids redissolved in dichloromethane upon shaking with 6 N HCl. The lactone acids were apparently hindered with respect to the acid such that they were chromato-

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graphed along with other products with 30% ethyl acetate/hexane (MPLC). The methyl esters of the lactone acids were prepared by treatment with diazomethane after chromatography.

(3aα,5aα,8aS*)-3,3,6,6-Tetraphenyl-2,7-dioxacyclopenta[a]pentalene-1,8-dione (15): mp 248–249 °C; IR (KBr) 3080, 3060, 3030, 2970, 2930, 1785, 1763 (strongest C=O), 1597, 1493, 1448, 1322, 1290, 1270, 1210, 1170, 1150, 1045, 1031, 1015, 998, 975, 757, 697 cm^{-1}; ^1H NMR δ 7.60–7.15 (m, 20 H), 4.08 (m, 2 H), 1.70 (m, 2 H), 1.30 (m, 2 H); ^{13}C NMR 171.3, 143.5, 141.5, 128.5, 128.0, 127.5, 125.9, 125.2, 125.0, 90.5, 65.9, 56.6, 32.3; MS exact mass calcd for $C_{33}H_{26}O_4$ m/z 486.1824, found 486.1852.

Hexahydro-6a-carboxy-3,3-diphenyl-6-(diphenylmethylene)-1H-cyclopenta[c]furan-1-one (17a): IR (KBr) 3420, 3050, 3020, 2955, 2920, 1773, 1730, 1597, 1492, 1450, 1260, 1150, 1090, 1045, 1030, 970, 760, 697 cm^{-1}; ^1H NMR δ 7.7–7.1 (m, 20 H), 5.4–5.0 (br s, 1 H), 4.27 (dd, J = 4.6, 7.2 Hz, 1 H), 2.67 (m, 1 H), 2.30 (m, 1 H), 1.88 (m, 1 H), 1.50 (m, 1 H); MS (m – 44(CO_2))/z 442.

Hexahydro-6a-carbomethoxy-3,3′-diphenyl-6-(diphenylmethylene)-1H-cyclopenta[c]furan-1-one (17a methyl ester): IR (KBr), 3060, 3020, 2950, 1787, 1735, 1595, 1490, 1450, 1255, 1145, 1030, 975, 760, 700 cm^{-1}; ^1H NMR δ 7.6–7.1 (m, 20 H), 4.26 (dd, J = 5.8, 7.2 Hz, 1 H), 2.72 (m, 1 H), 2.38 (s, 3 H), 2.32 (m, 1 H), 1.77 (m, 1 H), 1.35 (m, 1 H); MS exact mass calcd for $C_{34}H_{28}O_4$ m/z 500.1988, found 500.2006.

Hexahydro-3,3-diphenyl-6-(diphenylmethylene)-1H-cyclopenta[c]furan-1-one (18a – H_2O): mp 226–226.5 °C; IR (KBr) 3085, 3060, 3025, 2955, 2922, 1766, 1598, 1495, 1450, 1443, 1242, 1213, 1190, 1152, 1090, 965, 935, 758, 698 cm^{-1}; ^1H NMR δ 7.65–7.10 (m, 10 H), 3.79 (dt, J = 6.7, 8.0 Hz, 1 H), 3.66 (d, J = 6.8 Hz, 1 H), 2.50 (dt, J = 8.8, 17.6 Hz, 1 H), 2.32 (ddd, J = 3.7, 10.1, 17.6 Hz, 1 H), 1.78 (m, 1 H), 1.50 (m, 1 H); MS calcd for $C_{32}H_{26}O_2$ m/z 442.1934, found 442.1932.

(3aα,5aβ,8aS*)-3,3,6,6-Tetramethyl-2,7-dioxacyclopenta[a]pentalene-1,8-dione (16): mp 178.5–179 °C; IR (KBr) 2983, 2950, 1770, 1743 (strongest C=O) 1450, 1388, 1312, 1268, 1233, 1185, 1168, 1142, 1100, 1022, 960, 907 cm^{-1}; ^1H NMR δ 2.9–2.8 (m, 2 H), 2.1–1.9 (m, 2 H), 1.80–1.55 (m, 2 H), 1.70 (s, 6 H), 1.42 (s, 6 H); ^{13}C NMR 173.2, 85.0, 67.4, 57.0, 30.5, 30.3, 23.8 (57.0, 30.3, and 23.8 are negative with Attached Proton Test and therefore bear an odd number of hydrogens); MS exact mass calcd for $C_{13}H_{18}O_4$ 238.1205, found 238.1205.

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Registry No. (±)-**4s-s**, 94842-23-6; (±)-**4u**, 94842-24-7; (±)-**4s-a**, 94842-25-8; (±)-**5s-s**, 94842-26-9; (±)-**5u**, 94842-27-0; (±)-**5s-a**, 94842-28-1; (±)-**6s-s**, 94800-14-3; (±)-**6u**, 94842-29-2; (±)-**6s-a**, 94842-30-5; (±)-**7s-s**, 94842-31-6; (±)-**7u**, 94842-32-7; (±)-**7s-a**, 94902-02-0; (±)-**8s-s**, 94842-33-8; (±)-**8u**, 94842-34-9; (±)-**8s-a**, 94842-35-0; **9**, 89536-28-7; **10**, 55775-73-0; **11**, 4372-10-5; **12**, 89536-31-2; **13**, 89615-14-5; (±)-**14u**, 94800-15-4; (±)-**14s-a**, 94842-36-1; **15**, 94800-16-5; **16**, 94800-19-8; (±)-**17a**, 94800-17-6; (±)-**17a** (methyl ester), 94800-21-2; (±)-**17b**, 94800-20-1; (±)-**17b** (methyl ester), 94800-22-3; $CH_3(CH_2)_3CH{=}CH_2$, 592-41-6; $CH_3(CH_2)_5CH{=}CH_2$, 111-66-0; $(CH_3)_3CCH{=}CH_2$, 558-37-2; $PhC(CH_3){=}CH_2$, 98-83-9; $ClCH_2CH{=}CH_2$, 107-05-1; $Ph_2C{=}CH_2$, 530-48-3; $(CH_3)_2C{=}CH_2$, 115-11-7; $CH_2{=}CH_2$, 74-85-1; $Ph_2C{=}CH(CH_2)_2CH{=}CPh_2$, 70671-93-1; $(CH_3)_2C{=}CH(CH_2)_2C{-}H{=}C(CH_3)_2$, 16736-42-8; $Mn(OAc)_3$, 993-02-2; $CH_2(CO_2H)_2$, 141-82-2; (±)-*cis*-hexahydro-3,3-diphenyl-6-(diphenylmethylene)-1*H*-cyclopenta[*c*]furan-1-one, 94800-18-7; methylenecyclohexane, 1192-37-6; cyclohexene, 110-83-8; cyclopentene, 142-29-0.

Thermolysis of Molecules Containing NO_2 Groups[1]

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MINDO/3 calculations are reported for the thermal decomposition of nitromethane, methyl nitrite, methyl nitrate, nitroethylene, 1,1-dinitroethylene, *cis*-1,2-dinitroethylene, tetranitroethylene, nitroacetylene, and dinitroacetylene. The nitro compounds decompose most easily by first rearranging to isomeric nitrites. Methyl nitrite and methyl nitrate can decompose by fission into radicals ($CH_3O\cdot$ + ·NO or ·NO_2) or by alternative routes involving cyclic elimination ($CH_3ONO \rightarrow CH_2O + HONO$) or intermolecular transfer of oxygen ($CH_3ONO_2 + HCH_2ONO_2 \rightarrow CH_3ONO + HOCH_2ONO_2$). In the case of methyl nitrate, the latter alternative is likely to be favored under the conditions of a detonation shock wave. The activation energies calculated for the nitro → nitrite rearrangements of tetranitroethylene and of dinitroacetylene suggest that neither will be thermally stable.

Introduction

Reactions involving the thermolytic cleavage of bonds to form pairs of radicals have been extensively studied in recent years, partly because of their interest in connection with theories of unimolecular reactions and partly as a source of information concerning the heats of formation of radicals and bond dissociation energies (BDE). It is generally assumed that radical combination normally takes place without activation. If so, the observed activation energy for a bond dissociation process is equal to the BDE, while the heats of formation of the radicals formed are equal to that of the parent molecule *plus* the BDE.

Compounds containing the NO_2 group have been of especial interest in this connection, partly because they undergo thermal decomposition at relatively low temperatures and partly because of the role such decompositions play in the detonation of explosives. The activation energies for decomposition into radicals are moreover expected to be low because of the exceptional stability of nitric oxides (·NO) and nitrogen dioxide (·NO_2). The easy

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