General Synthesis of 1-Oxaspiro[4.5]decan-2-ones and 1-Oxaspiro[4.5]decanes from 5-Methylene-2(5*H*)-furanone

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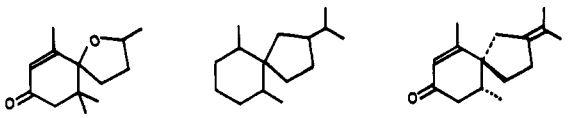
5-Methylene-2(5*H*)-furanone underwent Diels–Alder cycloadditions to butadiene and several acyclic and cyclic C-substituted dienes, respectively, affording bicyclic and tricyclic spiroadducts in good yields. These compounds are precursors of other unsaturated and saturated spirolactones and also spiroethers, which were obtained through simple chemical reactions, i.e., hydrogenation of C–C double bonds, reduction of the carbonyl group, and Michael addition. The synthesis of 32 spirolactones and eight spiroethers illustrates the scope and efficiency of this method. Many of these products are suitable for use as components of perfumes and aromas owing to their olfactive properties.

Introduction

Natural products containing the spiro[4.5]decane ring system are widespread,[1] several of them being well-known by their interesting olfactive properties. Some specific examples include theaspirone (1)[2] and sesquiterpenes structurally related to spirovetivanes (2), e.g., β-vetivone (3),[3] which are constituents of vetiver oil. Also, spirocyclic



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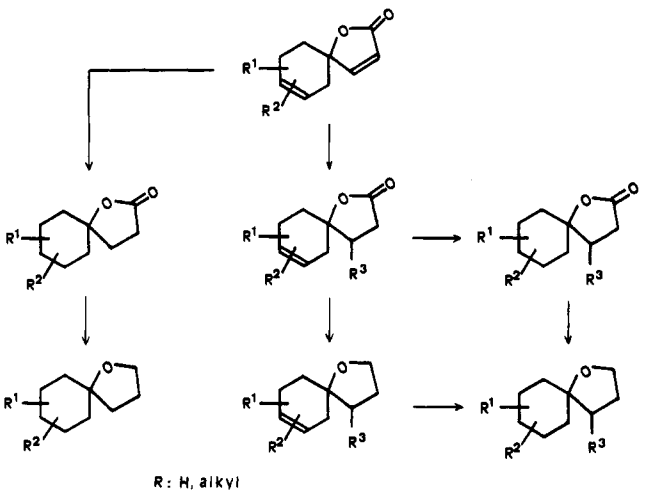
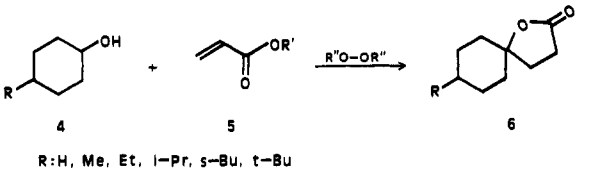
compounds (naturally occurring or from synthetic origin) serve as useful intermediates for the construction of other systems.[1a]

Such properties have prompted perfume and aroma specialized companies to achieve convenient methods in order to prepare suitable and useful spirocompounds. Among them, lactones and ethers are prominent.[4]

Although several methods have been reported,[4-13] the main described synthetic procedure to obtain saturated spirolactones 6 involves the radical reaction of an alkylcyclohexanol 4 and an alkyl acrylate 5 (eq 1).[4a,c] De-

Scheme I





4 5 6

R: H, Me, Et, i-Pr, s-Bu, t-Bu

pending on R, the odor of these compounds varies from creamy, lactone, or coumarin undertones to a wooden tonality accompanied by peach, apricot, or amber notes.[4a]

Furthermore, Weyerstahal et al. have published the synthesis of several saturated and unsaturated spirolactones and spiroethers starting, alternatively, from 4-methylcyclohexanone or 4-methylcyclohexenone and an alkyl Grignard reagent.[10]

However, these methods lack versatility because of the limited availability of the alkylcyclohexane precursors. Thus, in spite of the numerous syntheses already published, it was necessary to find a general entry to a variety of these spiro compounds.

We have shown recently that 5-methylene-2(5*H*)-furanone (protoanemonin; 7) behaves as a good dienophile in Diels–Alder reactions. Doubly unsaturated spirolactones are formed in high yields as a result of the excellent site selectivity observed in those cycloadditions (eq 2).[14] The

(1) For reviews on the occurrence, properties, structures, and synthesis of spirocyclic compounds, see: (a) Heathcock, C. H. *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1973; Vol. 2, pp 466–474 and 504–514. (b) Marshall, J. A.; Brady, S. F.; Andersen, N. H. *Fortschr. Chem. Org. Naturst.* **1974**, *31*, 283. (c) Krapcho, P. A. *Synthesis* **1978**, *77*. (d) Vandewalle, M.; De Clercq, P. *Tetrahedron* **1985**, *41*, 1767.

(2) Ina, K.; Sakato, Y.; Fukami, H. *Tetrahedron Lett.* **1968**, 2777.

(3) Marshall, J. A.; Johnson, P. C. *J. Am. Chem. Soc.* **1967**, *89*, 2750.

(4) (a) Dahill, R. T.; Golle, E. F.; Purzycki, K. Eur. Pat. Appl. EP 105,157, 11 Apr 1984. (b) Giersch, W. K.; Ohloff, G. Eur. Pat. Appl. EP 100,935, 22 Feb 1984. (c) Delay, F.; Giersch, W. K.; Ohloff, G. Eur. Pat. Appl. EP 200,890, 17 Dec 1986.

(5) Eaton, P. E.; Cooper, G. F.; Johnson, R. C.; Mueller, R. H. *J. Org. Chem.* **1972**, *37*, 1947.

(6) Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 5321.

(7) (a) Shulte-Elte, K. H.; Umiker, T.; Ohloff, G. *Helv. Chim. Acta* **1980**, *63*, 284. (b) Maurer, B.; Hauser, W.; Thommen, W.; Shulte-Elte, K. H.; Ohloff, G. *Ibid.* **1980**, *63*, 293.

(8) (a) Canonne, P.; Foscolos, G. B.; Bélanger, D. *J. Org. Chem.* **1980**, *45*, 1828. (b) Canonne, P.; Bélanger, D.; Lemay, G.; Foscolos, G. B. *Ibid.* **1981**, *46*, 3091. (c) Canonne, P.; Bélanger, D.; Lemay, G. *Ibid.* **1982**, *47*, 3953.

(9) Tanikaga, R.; Nozaki, Y.; Tanaka, K.; Kaji, A. *Chem. Lett.* **1982**, 1703.

(10) Buchmann, B.; Marschall-Weyerstahl, H.; Weyerstahl, P. *Tetrahedron* **1984**, *40*, 3393.

(11) Schlect, M. F.; Kim, H. J. *Tetrahedron Lett.* **1985**, *26*, 127.

(12) Mandal, A. K.; Jawalkar, D. G. *Tetrahedron Lett.* **1986**, *27*, 99.

(13) Buchwald, S. L.; Fang, Q.; King, S. M. *Tetrahedron Lett.* **1988**, *23*, 3445.

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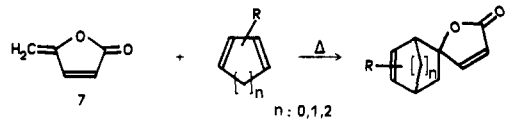


regioselectivity in the reactions with unsymmetrically substituted dienes[14a] and the endo/exo stereoselectivity with cyclopentadiene and cyclohexadiene have also been investigated and rationalized.[15]

We report in this article the Diels–Alder cycloadditions of protoanemonin (7) to butadiene and several kinds of C-substituted dienes. The adducts thus obtained underwent simple chemical transformations providing an easy, efficient, and inexpensive synthetic approach to a wide range of spirolactones and spiroethers.

Results and Discussion

Three simple procedures are described in the literature to prepare protoanemonin (7). They begin, alternatively, from levulinic acid[16a,b] or 5-(hydroxymethyl)furfural[16c] as cheap easily available starting materials, thereby allowing the following synthetic procedures to be carried out on a multigram scale.

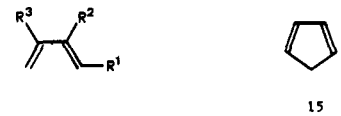
Diels–Alder cycloadditions of 7 to different dienes, including cyclic and acyclic structures (see below), gave bicyclic and tricyclic adducts (Scheme I). These compounds were precursors of other saturated and unsaturated spirolactones, which were obtained through chemical transformations involving the following: (a) total hydrogenation of the C–C double bonds, (b) selective reduction of the conjugated C–C double bond, (c) alkylation by means of conjugate addition of an organocuprate. In addition, reduction of the carbonyl group in these spirolactones led to the formation of diols, which were cyclized to spiroethers. Scheme I summarizes the synthetic pathways from adducts obtained through reaction of 7 and acyclic dienes.

1. **Spirolactones.** Dienophile 7 underwent reaction with acyclic dienes including 1,3-butadiene (8), isoprene (9), piperylene (10), 2,3-dimethyl-1,3-butadiene (11), 2-methyl-1,3-pentadiene (12), 3-methyl-1,3-pentadiene (13), and myrcene (14) (Chart I), respectively, at temperatures between 130–155 °C, giving the bicyclic spiroadducts **19–25** (Chart II) in 70–85% yields, but with diene 14 the yield was 49%. Experimental conditions are summarized in Table I.

Moreover, 7 reacted with cyclopentadiene (15), cyclohexadiene (16), α-terpinene (17), and α-phellandrene (18) (Chart I), respectively, to afford the tricyclic adducts **41–44**, **48**, and **49** (Chart II). Reaction of 7 with excess diene 15 was carried out at 90 °C for 2 h, giving the stereoisomers **41** and **43** (70:30 ratio determined by GC), easily isolated by column chromatography, in 75% total yield. In a similar manner, 7 was reacted with 16 in CH_2Cl_2 at 165 °C for 2 h, affording a 70:30 mixture of adducts **42**/**44**, which were separated by column chromatography. Mixtures of regio- and diastereoisomers were obtained in the reactions of 7 with dienes 17 and 18, respectively, but no effort was made to separate them.

Many of these adducts were submitted to several transformations resumed as follows:

Chart I



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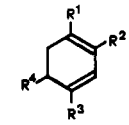
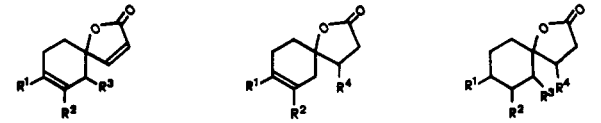


	R^1	R^2	R^3
8:	H	H	H
9:	H	Me	H
10:	Me	H	H
11:	H	Me	Me
12:	Me	H	Me
13:	Me	Me	H
14:	H	$(CH_2)_2CH=C(Me)_2$	H

	R^1	R^2	R^3	R^4
16:	H	H	H	H
17:	Me	H	i-Pr	H
18:	H	Me	H	i-Pr

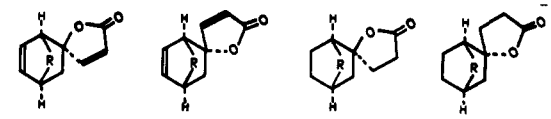
Chart II



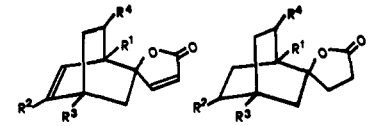
	R^1	R^2	R^3
19:	H	H	H
20:	Me	H	H
21:	H	H	Me
22:	Me	Me	H
23:	Me	H	Me
24:	H	Me	Me
25:	$(CH_2)_2CH=C(Me)_2$	H	H

	R^1	R^2	R^4
26:	H	H	H
27:	Me	H	H
28:	Me	Me	H
29:	H	H	Me
30:	Me	H	Me
31:	Me	Me	Me

	R^1	R^2	R^3	R^4
32:	H	H	H	H
33:	Me	H	H	H
34:	H	H	Me	H
35:	Me	Me	H	H
36:	Me	H	Me	H
37:	H	Me	Me	H
38:	H	H	H	Me
39:	Me	H	H	Me
40:	$(CH_2)_3CH(Me)_2$	H	H	H



R = CH_2	41	43	45	47
R = $(CH_2)_2$	42	44	46	



R^1 = Me, R^2 = R^4 = H, R^3 = $CH(Me)_2$	48	50
R^1 = R^3 = H, R^4 = $CH(Me)_2$, R^2 = Me	49	51

Table I. Diels–Alder Cycloadditions of 7 with Dienes

diene	diene/7 molar ratio	solvent	T (°C)	time (h)	adduct(s)	yield[a] (%)
8	45		155	4	**19**	85
9	45		154	4	**20**[b]	75
10	45		150	4	**21**[c]	64
11	45		162	4	**22**	79
12	45		159	4	**23**[c]	78
13	45		130	18	**24**[c]	73
14	45		157	3	**25**[b]	49
15	4	CH_2Cl_2	90	2	**41/43**	75
16	4	CH_2Cl_2	165	2	**42/44**	80
17	12	toluene	145	23	**49**[d]	56
18	3.3	toluene	145	16	**50**[d]	71

[a] Isolated yields. [b] Major regioisomer. [c] Mixture of diastereoisomers. [d] Mixture of regio- and diastereoisomers (one isomer shown).

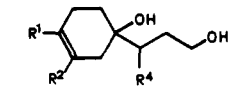
(a) *Total catalytic hydrogenation*, leading to saturated spirolactones. Hydrogenation of adducts **19–25**, **41–44**, **48**,

(14) (a) Alonso, D.; Ortí, J.; Branchadell, V.; Oliva, A.; Ortuño, R. M.; Bertrán, J.; Font, J. *J. Org. Chem.* **1990**, *55*, 3060. (b) Branchadell, V.; Ortí, J.; Ortuño, R. M.; Oliva, A.; Font, J.; Bertrán, J.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 2190.

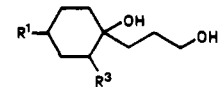
(15) Alonso, D.; Branchadell, V.; Font, J.; Oliva, A.; Ortuño, R. M.; Sánchez-Ferrando, F. *Tetrahedron* **1990**, *46*, 4371.

(16) (a) Shaw, E. *J. Am. Chem. Soc.* **1946**, *68*, 2510. (b) Grundman, C.; Kober, F. *Ibid.* **1955**, *77*, 2332. (c) Alibés, R.; Font, J.; Mulà, A.; Ortuño, R. M. *Synth. Commun.* **1990**, *20*, 2607.

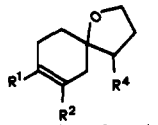
Chart III



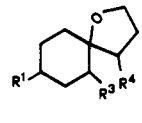
	R^1	R^2	R^4
52:	H	H	H
53:	H	H	Me
54:	Me	H	Me
55:	Me	Me	H
56:	Me	Me	Me



	R^1	R^3
57:	H	H
58:	Me	H
59:	H	Me



	R^1	R^2	R^4
60:	H	H	H
61:	H	H	Me
62:	Me	H	Me
63:	Me	Me	Me



	R^1	R^3	R^4
64:	H	H	H
65:	Me	H	H
66:	H	H	Me
67:	Me	H	Me

and **49**, at 2–3 atm of pressure and rt, using 10% Pd/C as a catalyst, yielded almost quantitatively compounds **32–40**, **45–47**, **50**, and **51** (Chart II).

(b) *Selective reduction of the conjugated C–C double bond*, affording spirolactones with one unsaturation in the six-membered ring. This transformation was performed by partial hydrogenation, at atmospheric pressure and control of the hydrogen consumption, of adduct **22** to give **28** in quantitative yield. Alternatively, this product was prepared by selective reduction using Red-Al (Vitride) in the presence of cuprous bromide and 2-butanol.[17] This method also allowed the preparation of **26** and **27** from adducts **19** and **20**, respectively (Chart II). Yields ranged from 75 to 90%.

(c) *Michael addition of an organocuprate*, providing spiranes containing an alkylcyclohexene ring and a β-alkyl-substituted butyrolactone. Lithium dimethylcuprate was chosen, owing to its easy preparation, to perform this type of process. Addition of adducts **19**, **20**, and **22** to an ethereal solution of this reagent at −20 °C gave, respectively, compounds **29**, **27**, and **31**, in 65–85% yields.

2. Spiroethers. Conversion of the butyrolactones into tetrahydrofuran derivatives was realized through reductive lactone opening with $LiBH_4$. The diol thus obtained was cyclized in situ, via selective tosylation of the primary alcohol.[18] The overall yield of this process was 60–85%. Diols **52–59** were prepared in this way from lactones **26**, **29**, **30**, **28**, **31**, **32**, **33**, and **34**, respectively. In turn, diols **52–54** and **56–58** reacted with tosyl chloride in pyridine to afford the corresponding ethers **60–65** (Chart III).

Moreover, catalytic hydrogenation of the C–C double bond in **61** and **62** yielded the saturated spiroethers **66** and **67**, respectively.

3. Olfactive Properties. The spiranes prepared in this work generally showed olfactive properties, and the following products are fruity volatile notes with a persistent background of light coumarin undertone. The additional methyl group in **23** introduces a tonality of jasmine accompanied by rose, in the end notes. Compound **20** has been used in the preparation of a "Fougère-type" cologne for men.[19] In contrast, lactone **43** has a sweet odor of vanilla and milk, reminiscent of caramel cream. Furthermore, the spiroethers **62**, **65**, and **67** have a similar olfactive character. Ether **65** possesses a flowery–fruity odor with a turpentine undertone. The additional methyl group introduces here a tonality of herbal green accompanied by eucalyptus in **62**, and by anis in **67**.

Conclusions

We have described in this paper easy and useful synthetic methodologies that allow the preparation of several kinds of spirolactones and spiroethers from a common precursor: an adduct of protoanemonin and a convenient diene. These syntheses compete advantageously with other procedures previously reported in the literature, due to their simplicity and the availability of the starting materials. The efficiency of these methods is illustrated by the preparation of 33 spirolactones and eight spiroethers. Many of these compounds show interesting olfactive properties as constituents of aromas and fragrances.

Experimental Section

Melting points were determined on a hot stage and are uncorrected. Distillation of small amounts was effected on a rotary distillation apparatus (only the oven temperature is given). The electron-impact mass spectra were recorded at 70 eV.

General Procedures. (a) Diels–Alder Cycloadditions. All reactions were performed in sealed tubes. Cycloadditions of protoanemonin (**7**) to the dienes **8–14** were conducted using 1 mmol of dienophile, 45 mmol of the freshly distilled diene, and a trace of hydroquinone, at temperatures between 130–162 °C (Table I). Reaction time was 4 h for **8–12**. The reactions with dienes **13** and **14** were carried out for 18- and 3-h periods, respectively. Reactions of **7** with cyclopentadiene (**15**) and cyclohexadiene (**16**) were effected using 4 mmol of **7** and 16 mmol of diene in 16 mL of CH_2Cl_2 (0.6 M in **7**). Cycloaddition to α-terpinene (**17**) was performed at 145 °C for 16 h using 20 mmol of **7** and 240 mmol of **17** in 50 mL of toluene (0.4 M in **7**). Reaction with α-phellandrene (**18**) was accomplished at 145 °C for 16 h, from 20 mmol of **7** and 66 mmol of **18** in 50 mL of toluene (0.4 M in **7**; Table I). The adducts were purified by column chromatography on silica gel, using mixtures of hexane–ethyl acetate as eluents. The major adducts from the reactions of **7** with **9** (regioisomer **20**) and **12**, as well as the endo/exo stereoisomers from the reactions with **15** and **16**, respectively, were thus isolated.

(b) Catalytic Hydrogenations. Solutions (0.1 M) of the corresponding substrates were hydrogenated at 1–2 atm of pressure using 10% Pd/C. The crude products were purified by distillation or by column chromatography on silica gel, using mixtures of hexane–ethyl acetate as eluents.

(c) Selective Reduction of the Conjugated C–C Bond by Means of a Modified Hydride.[17] To a solution of CuBr (3.9 g, 27 mmol) in 50 mL of THF, cooled at 0 °C, was added 16 mL of a 3.4 M solution of Vitride (aluminum and sodium bis(2-methoxyethoxy)hydride, 55 mmol). The mixture was stirred at 0 °C for 30 min and cooled at −78 °C, and then 1-butanol (5.63 mL, 61.5 mmol) was added. To this mixture was added dropwise a solution of the conjugated spirolactone (3.4 mmol) in THF (9 mL). After 15 min the mixture was warmed to −20 °C and stirred for 2 h. Then, water (9 mL) was added and the resulting mixture poured into saturated aqueous NH_4Cl (250 mL). The aqueous layer was extracted with ether (3 × 150 mL), and the combined extracts were washed with water (75 mL) and dried. The crude product was purified by distillation at reduced pressure.

(17) (a) Semmelhack, M. F.; Stauffer, R. D.; Yamashita, A. *J. Org. Chem.* **1977**, *42*, 3180. (b) Semmelhack, M. F.; Stauffer, R. D. *Ibid.* **1975**, *40*, 3619.

(18) Drew, M. G. B.; Mann, J.; Thomas, A. *J. Chem. Soc., Perkin Trans. 1* **1986**, 2279.

(19) Alonso, D.; Font, J.; Ortuño, R. M. Span. Pat. Appl. 8,801,701, 30 May 1988.

(d) Michael Addition of Lithium Dimethylcuprate. To a stirred solution of lithium dimethylcuprate (32 mmol) in ether (160 mL), cooled at −35 °C, was added dropwise the conjugated spirolactone (13 mmol) in ether (35 mL). The mixture was stirred at −20 °C for 30 min, and then saturated NH_4Cl (80 mL) was added and the stirring continued for 15 min to warm the mixture to rt. Salts were filtered off, the layers were separated, and the aqueous phase was extracted with ethyl acetate (3 × 150 mL). The combined extracts were washed with brine and dried. The crude Michael adducts were purified by distillation.

(e) Reduction of the Lactones to Diols.[18] To a solution of the spirolactone (1.5 mmol) in THF (6 mL) was added a 2 M solution of $LiBH_4$ (0.7 mL, 1.4 mmol), and the resulting mixture was stirred at rt for 36 h. The mixture was hydrolyzed (10 mL), and the solution thus obtained was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were washed with water (2 × 20 mL) and dried. The crude diols were purified by distillation.

(f) Conversion of Diols in Spiroethers.[18] To a stirred solution of the diol (3.4 mmol) in 8.5 mL of anhydrous pyridine, cooled at 0 °C, was added dropwise a solution of TsCl (3.6 mmol) in 6.5 mL of anhydrous pyridine. The mixture was stirred at 0 °C for 1.5 h and at rt for 1.5 h. Then, the mixture was poured into ice–water (60 mL) and extracted with ether (3 × 100 mL). The combined organic extracts were washed with 5% HCl (50 mL) and water (75 mL) and dried. The crude spiroethers were purified by distillation.

Cycloadducts **19**, **30**, **32–34**, **38**, **39**, **54**, **57**, **58**, **60**, **62**, **64**, **65**, and **67** are known compounds. Their IR, ^1H NMR, and ^{13}C NMR spectral data agree with the literature values, when described. Compounds **20–23** and **41–44** have been prepared for the first time in our laboratory and published in previous papers.[14a,15]

1-Oxaspiro[4.5]deca-3,7-dien-2-one (19):[9] yield 0.22 g (85%); mp 65–66 °C (lit.[9] 66–67 °C). Undescribed spectral data: IR (KBr) 1758, 1654 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 1.77 (1 H, m), 1.92 (1 H, m), 2.11–2.42 (4 H, complex absorption), 5.64 (1 H, m), 5.79 (1 H, m), 6.03 (1 H, d, J = 5.59 Hz), 7.47 (1 H, d, J = 5.59 Hz); 20-MHz ^{13}C NMR ($CDCl_3$) δ 22.9, 30.7, 33.6, 86.5, 120.2, 122.4, 126.2, 159.3, 171.8; MS m/e (relative intensity) 150 (M, 5.0), 68 (24.6), 54 (100).

8-Methyl-1-oxaspiro[4.5]deca-3,7-dien-2-one (20):[14a] yield 70 g (75%); bp 84 °C (0.1 Torr).

6-Methyl-1-oxaspiro[4.5]deca-3,7-dien-2-one (21).[14a] Mixture of diastereoisomers (75:25; GC): yield 3.6 g (72%); oven temperature 90–95 °C (0.04 Torr).

7,8-Dimethyl-1-oxaspiro[4.5]deca-3,7-dien-2-one (22):[14a] yield 25 g (81%); bp 113 °C (0.02 Torr).

6,8-Dimethyl-1-oxaspiro[4.5]deca-3,7-dien-2-one (23).[14a] Mixture of diastereoisomers (80:20; GC): yield 34 g (80%); bp 90–91 °C (0.07 Torr).

6,7-Dimethyl-1-oxaspiro[4.5]deca-3,7-dien-2-one (24). Mixture of diastereoisomers (80:20; GC), yield 1.2 g (73%). The major diastereoisomer was isolated through recrystallization of the mixture, mp (ether–pentane) 78–79 °C. Its spectral data follow: IR (film) 1751, 1600 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.00 (3 H, d, J = 7.30 Hz), 1.73 (3 H, d, J = 1.20 Hz), 1.89 (2 H, m), 2.00–2.60 (3 H, complex absorption), 5.49 (1 H, m), 6.10 (1 H, d, J = 6.08 Hz), 7.50 (1 H, d, J = 6.08 Hz); 20-MHz ^{13}C NMR ($CDCl_3$) δ 14.6, 21.1, 23.1, 29.0, 41.4, 90.5, 120.4, 121.2, 134.6, 158.3, 171.8. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.23; H, 8.02.

8-(4-Methyl-3-pentenyl)-1-oxaspiro[4.5]deca-3,7-dien-2-one and 7-(4-Methyl-3-pentenyl)-1-oxaspiro[4.5]deca-3,7-dien-2-one (25). Mixture of regioisomers (70:30; NMR, GC); the major regioisomer is shown: yield 10 g (49%); oven temperature 105–115 °C (0.01 Torr); IR (film) 1763, 1673, 1648, 1603 cm^{-1}; MS m/e 233 (M + 1, 7.3), 164 (59.6), 69 (72.8), 41 (100); 80-MHz ^1H NMR ($CDCl_3$) δ 1.62 (3 H, br s); 1.68 (3 H, br s); 1.78–2.43 (10 H, complex absorption), 5.08 (1 H, br s), 5.37 and 5.52 (1 H, br s), 6.03 (1 H, d, J = 5.60 Hz), 7.47 (1 H, d, J = 5.60 Hz). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.32; H, 8.65.

1-Oxaspiro[4.5]dec-7-en-2-one (26): yield 0.47 g (91%); oven temperature 70–75 °C (0.05 Torr); IR (film) 1770, 1654 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.66–2.46 (6 H, complex absorption), 2.05 (2 H, m), 2.64 (2 H, m), 5.67 (2 H, m); 20-MHz ^{13}C NMR ($CDCl_3$) δ 22.8, 28.2, 32.1, 32.2, 36.4, 84.2, 123.0, 126.3, 176.2. Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.99; H, 8.01.

8-Methyl-1-oxaspiro[4.5]dec-7-en-2-one (27): yield 0.18 g (87%); oven temperature 115 °C (0.07 Torr); IR (film) 1770, 1678 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.68 (3 H, d, J = 1.41 Hz), 2.02 (2 H, m), 1.78–2.41 (6 H, complex absorption), 2.62 (2 H, m), 5.27 (1 H, m); 20-MHz ^{13}C NMR ($CDCl_3$) δ 22.7, 27.6, 28.3, 32.1, 32.6, 36.6, 84.2, 117.2, 133.6, 176.2. Anal. Calcd for $C_9H_{12}O_2$: C, 72.26; H, 8.49. Found: C, 72.25; H, 8.69.

7,8-Dimethyl-1-oxaspiro[4.5]dec-7-en-2-one (28): yield 0.7 g (72%); oven temperature 120 °C (0.1 Torr); IR (film) 1770 cm^{-1}; MS m/e (relative intensity) 181 (M + 1, 25.3), 180 (M, 25.9), 165 (8.9), 82 (70.1), 67 (87.1), 55 (50.8), 41 (100); 80-MHz ^1H NMR ($CDCl_3$) δ 1.64 (6 H, s), 1.72–1.91 (2 H, complex absorption), 2.04 (2 H, m), 2.23 (4 H, m), 2.63 (2 H, m); 20-MHz ^{13}C NMR ($CDCl_3$) δ 18.2, 18.7, 28.3, 29.1, 32.2, 32.9, 42.6, 85.0, 121.9, 125.1, 176.3. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.16; H, 9.07.

4-Methyl-1-oxaspiro[4.5]dec-7-en-2-one (29). Mixture of diastereoisomers: yield 1.65 g (78%); oven temperature 98 °C (0.05 Torr); IR (film) 1774, 1657 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.09 (3 H, d, J = 5.6 Hz), 1.35–3.04 (9 H, complex absorption), 5.68 (2 H, m). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.12; H, 8.68.

4,8-Dimethyl-1-oxaspiro[4.5]dec-7-en-2-one (30).[10] Mixture of diastereoisomers: yield 0.47 g (85%); oven temperature 92 °C (0.05 Torr) (lit.[10] bp 135 °C (4 Torr)).

4,7,8-Trimethyl-1-oxaspiro[4.5]dec-7-en-2-one (31). Mixture of diastereoisomers: yield 0.76 g (67%); oven temperature 125 °C (0.05 Torr); IR (film) 1769 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.07 (d, J = 7.66 Hz) and 1.04 (d, J = 7.66 Hz) (3 H), 1.64 (6 H, s), 1.65–2.92 (9 H, complex absorption). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.94; H, 9.51.

1-Oxaspiro[4.5]decan-2-one (32):[5,10] yield 0.29 g (87%); oven temperature 60 °C (0.05 Torr) (lit.[5] oven temperature 50 °C (0.05 Torr), lit.[10] bp 80–110 °C (0.05 Torr)).

8-Methyl-1-oxaspiro[4.5]decan-2-one (33).[4a] Mixture of diastereoisomers, yield 0.27 g (99%), oven temperature 75 °C (0.02–0.05 Torr) (lit.[4a] bp 97–100 °C (0.5 Torr)). Previously undescribed spectra for the major isomer: IR (film) 1770 cm^{-1}; MS m/e (relative intensity) 169 (M + 1, 29.5), 168 (M, 6.8), 111 (100), 55 (52.1); 80-MHz ^1H NMR ($CDCl_3$) δ 0.97 (3 H, br s), 1.12–1.76 (9 H, m), 1.76–2.16 (2 H, m), 2.60 (2 H, m); 20-MHz ^{13}C NMR ($CDCl_3$) δ 21.5, 28.1, 30.2, 31.0, 33.6, 36.4, 84.9, 176.2.

6-Methyl-1-oxaspiro[4.5]decan-2-one (34).[20] Mixture of diastereoisomers, yield 1.5 g (99%). Undescribed characterization: oven temperature 75 °C (0.05 Torr); IR (film) 1775 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 0.89 (3 H, d, J = 6.37 Hz), 1.10–2.84 (13 H, complex absorption).

7,8-Dimethyl-1-oxaspiro[4.5]decan-2-one (35). Mixture of diastereoisomers: yield 3.34 g (100%); oven temperature 90 °C (0.07 Torr); IR (film) 1770 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 0.91 (6 H, m), 1.10–1.93 (8 H, complex absorption), 2.10 (2 H, m), 2.52 (2 H, m). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.52; H, 10.24.

6,8-Dimethyl-1-oxaspiro[4.5]decan-2-one (36). Mixture of diastereoisomers: yield 14.2 g (99%); oven temperature 76 °C (0.07 Torr); IR (film) 1770 cm^{-1}; MS m/e (relative intensity) 183 (M + 1, 11.8), 182 (M, 8.5), 111 (100); 80-MHz ^1H NMR ($CDCl_3$) δ 0.83–1.04 (6 H, complex absorption), 1.27–2.39 (10 H, complex absorption), 2.39–2.74 (2 H, complex absorption). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.10; H, 9.74.

6,7-Dimethyl-1-oxaspiro[4.5]decan-2-one (37). Mixture of diastereoisomers: yield 1.1 g (100%); oven temperature 130 °C (0.08 Torr); IR (film) 1770 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 0.87 (6 H, m), 1.08–2.32 (10 H, complex absorption), 2.54 (2 H, m). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.54; H, 10.28.

4-Methyl-1-oxaspiro[4.5]decan-2-one (38).[21] Mixture of diastereoisomers, yield 0.24 g (92%), oven temperature 80 °C (0.01 Torr). Undescribed spectra: IR (film) 1772 cm^{-1}; 80-MHz ^1H

(20) Nakamura, E.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1986**, *108*, 3745.
(21) Jacobson, R. M.; Clader, J. W. *Tetrahedron Lett.* **1980**, *21*, 1205.
(22) (a) Kaplan, L. J. Ger. Offen. DE 3,241,933, 26 May 1983; US Appl. 320,635, 12 Nov 1981. (b) Kaplan, L. J. US 4,438,130, 20 March 1984.

NMR ($CDCl_3$) δ 1.06 (3 H, d, J = 6.95 Hz), 1.67 (10 H, br s), 2.05–2.88 (3 H, complex absorption).

4,8-Dimethyl-1-oxaspiro[4.5]decan-2-one (39).[10] Mixture of diastereoisomers: yield 0.16 g (96%); oven temperature 95–100 °C (0.07 Torr) (lit.[10] bp 128 °C (4 Torr)).

8-Isohexyl-1-oxaspiro[4.5]decan-2-one and 7-Isohexyl-1-oxaspiro[4.5]decan-2-one (40). Mixture of isomers, the major regioisomer is shown: yield 8.5 g (98%); oven temperature 112–124 °C (0.02 Torr); IR (film) 1773 cm^{-1}; MS m/e 239 (M + 1, 14.1), 238 (M, 2.0), 112 (16.5), 111 (50.6), 81 (15.9), 69 (18.4), 67 (25.7), 55 (63.5), 53 (15.3); 80-MHz ^1H NMR ($CDCl_3$) δ 0.83 (6 H, d, J = 6.4 Hz), 1.0–2.16 (18 H, complex absorption), 2.54 (2 H, m). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.85; H, 11.21.

3-((1*R,2*S**,4*R**)-2-Hydroxybicyclo[2.2.1]hept-5-en-2-yl)propanoic acid 1,4-lactone (41):**[15] yield 1 g (22%); mp 95–97 °C.

3-((1*R,2*S**,4*R**)-2-Hydroxybicyclo[2.2.2]oct-5-en-2-yl)-propanoic acid 1,4-lactone (42):**[15] yield 1.1 g (54%); mp 51–52 °C.

3-((1*R,2*R**,4*R**)-2-Hydroxybicyclo[2.2.1]hept-5-en-2-yl)propanoic acid 1,4-lactone (43):**[15] yield 1 g (52%); mp 114–115 °C.

3-((1*R,2*R**,4*R**)-2-Hydroxybicyclo[2.2.2]oct-5-en-2-yl)-propanoic acid 1,4-lactone (44):**[15] yield 0.5 g (24%); mp 92–94 °C.

3-((1*R,2*R**,4*S**)-2-Hydroxybicyclo[2.2.1]heptan-2-yl)-propanoic acid 1,4-lactone (45):** yield 0.22 g (100%); oven temperature 80–85 °C (0.08 Torr); IR (film) 1770 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.04–1.72 (6 H, complex absorption), 1.72–2.74 (8 H, complex absorption); 20-MHz ^{13}C NMR ($CDCl_3$) δ 22.1, 28.0, 29.6, 30.5, 36.4, 37.6, 45.6, 46.3, 93.4, 176.5. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.89; H, 8.81.

3-(2-Hydroxybicyclo[2.2.2]oct-5-en-2-yl)propanoic acid 1,4-lactone (46): yield 0.37 g (100%); oven temperature 125–130 °C (0.2 Torr); IR (film) 1770 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.1–2.4 (14 H, complex absorption), 2.4–2.7 (2 H, complex absorption); 20-MHz ^{13}C NMR ($CDCl_3$) δ 20.7, 21.5, 23.9, 24.0, 25.2, 28.7, 33.6, 34.4, 41.0, 88.1, 176.6. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.09; H, 9.02.

3-((1*R,2*S**,4*S**)-2-Hydroxybicyclo[2.2.1]heptan-2-yl)-propanoic acid 1,4-lactone (47):** yield 0.40 g (100%); oven temperature 75–80 °C (0.08 Torr); mp (ether–pentane) 69–69 °C; IR (film) 1774 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.10–1.90 (8 H, complex absorption), 1.90–2.41 (4 H, complex absorption), 2.41–2.77 (2 H, complex absorption); 20-MHz ^{13}C NMR ($CDCl_3$) δ 21.8, 27.6, 28.9, 35.9, 36.1, 37.5, 44.2, 45.7, 91.6, 176.5. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.47; H, 8.58.

3-(1-Methyl-2-hydroxy-4-isopropylbicyclo[2.2.2]oct-5-en-2-yl)propanoic Acid 1,4-Lactone (48). Mixture of regio- and diastereoisomers; one isomer shown: yield 2.7 g (56%); oven temperature 104–106 °C (0.1 Torr); IR (film) 1762, 1600 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 0.69–1.00 (6 H, complex absorption), 1.15 (3 H, s), 1.16–1.92 (7 H, complex absorption), 5.78–6.02 (2 H, complex absorption), 6.20–6.34 (1 H, complex absorption), 7.06 (d, J = 5.12 Hz), 7.17 (d, J = 5.12 Hz), 7.18 (d, J = 5.12 Hz) and 7.52 (d, J = 5.12 Hz) (1H). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.62; H, 8.78.

3-(2-Hydroxy-5-methyl-7-isopropylbicyclo[2.2.2]oct-5-en-2-yl)propanoic Acid 1,4-Lactone (49). Mixture of regio- and diastereoisomers; one isomer shown: yield 3.3 g (70%); oven temperature 130–140 °C (0.03 Torr); IR (film) 1756, 1654, 1601 cm^{-1}; 80-MHz NMR ^1H ($CDCl_3$) δ 0.81 (6 H, d, J = 5.1 Hz), 1.64–2.17 (6 H, complex absorption), 1.82 (3 H, d, J = 1.91 Hz); 2.46 (2 H, m), 5.10 (m) and 5.70 (m) (1H), 5.88 (d, J = 5.74 Hz) and 5.99 (d, J = 5.74 Hz) (1H). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.62; H, 8.75.

3-(1-Methyl-2-hydroxy-4-isopropylbicyclo[2.2.2]oct-2-yl)-propanoic Acid 1,4-Lactone (50). Mixture of regio- and diastereoisomers; one isomer shown: yield 0.8 g (92%); oven temperature 88–94 °C (0.05 Torr); IR (film) 1773 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 0.73–1.05 (6 H, complex absorption), 1.05–2.00 (16 H, complex absorption), 2.54 (2 H, m). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.37; H, 10.39.

3-(2-Hydroxy-5-methyl-7-isopropylbicyclo[2.2.2]oct-2-yl)-propanoic Acid 1,4-Lactone (51). Mixture of regio- and diastereoisomers; one isomer shown: yield 1.2 g (94%), oven temperature 96–102 °C (0.05 Torr), IR (film) 1773 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 0.70–1.07 (9 H, complex absorption), 1.07–2.38 (13 H, complex absorption), 2.38–2.77 (2 H, complex absorption). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.38; H, 10.30.

1-(3-Hydroxypropyl)-3-cyclohexen-1-ol (52): yield 0.18 g (79%); oven temperature 120 °C (0.05 Torr); IR (film) 3565–3080 (ba), 1100 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.69 (6 H, m), 2.12 (4 H, m), 2.55 (2 H, s), 3.68 (2 H, m), 5.66 (2 H, m); 20-MHz ^{13}C NMR ($CDCl_3$) δ 22.8, 26.0, 33.1, 37.5, 37.9, 62.8, 69.7, 124.4, 126.3. Anal. Calcd for $C_9H_{16}O_2$: C, 69.20; H, 10.32. Found: C, 69.06; H, 10.52.

1-(3-Hydroxy-1-methylpropyl)-3-cyclohexen-1-ol (53). Mixture of diastereoisomers: yield 0.87 g (83%); oven temperature 140 °C (0.05 Torr); IR (film) 3580–3090 (ba), 1658 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.00 (3 H, m), 1.39–2.31 (9 H, complex absorption), 2.40 (2 H, s), 3.74 (2 H, m), 5.72 (2 H, m). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.21; H, 10.80.

4-Methyl-1-(3-hydroxy-1-methylpropyl)-3-cyclohexen-1-ol (54).[10] Mixture of diastereoisomers: yield 0.26 mg (94%); oven temperature 110 °C (0.05 Torr) (lit.[10] bp 80–120 °C (0.05 Torr)).

3,4-Dimethyl-1-(3-hydroxypropyl)-3-cyclohexen-1-ol (55): yield 0.24 g (81%); oven temperature 160 °C (0.05 Torr); IR (film) 3517–3019 (ba), 1107 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.62 (12 H, complex absorption), 2.03 (2 H, complex absorption), 3.67 (2 H, m); 20-MHz ^{13}C NMR ($CDCl_3$) δ 18.3, 18.9, 26.0, 29.0, 33.6, 37.4, 44.1, 62.5, 70.2, 122.8, 124.4. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 72.06; H, 11.17.

3,4-Dimethyl-1-(3-hydroxy-1-methylpropyl)-3-cyclohexen-1-ol (56). Mixture of diastereoisomers: yield 0.51 g (90%); oven temperature 170 °C (0.08 Torr); IR (film) 3578–3062 (ba), 1123, 1056 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 0.97 (3 H, m), 1.63 (6 H, s), 1.33–2.30 (9 H, complex absorption), 2.34 (2 H, s), 3.72 (2 H, m). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.60; H, 11.72.

1-(3-Hydroxypropyl)cyclohexanol (57):[5,8a] yield 0.25 g (85%); oven temperature 95 °C (0.02 Torr) (lit.[8a] bp 108–110 °C (0.03 Torr); lit.[5] bp 100 °C (0.04 Torr)).

4-Methyl-1-(3-hydroxypropyl)cyclohexanol (58).[10] Mixture of diastereoisomers: yield 0.35 g (98%); oven temperature 90 °C (0.01 Torr) (lit.[10] bp 110–150 °C (4 Torr)).

2-Methyl-1-(3-hydroxypropyl)cyclohexanol (59). Mixture of diastereoisomers: yield 0.44 g (89%); oven temperature 125 °C (0.05 Torr); IR (film) 3578–3043 (ba), 1107, 1057 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 0.95 (3 H, d, J = 6.1 Hz), 1.08–2.00 (15 H, complex absorption), 2.14 (3 H, br s), 3.68 (2 H, m). Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.77; H, 11.89.

1-Oxaspiro[4.5]dec-7-ene (60).[19] Yield, 0.09 g (77.8%); oven temperature 90 °C (10 Torr). Previously undescribed spectral data: IR (film) 1653, 1105 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.56–2.29 (10 H, complex absorption), 3.87 (2 H, t, J = 6.35 Hz), 5.65 (2 H, m); 20-MHz ^{13}C NMR ($CDCl_3$) δ 24.1, 25.6, 32.8, 36.1, 37.4, 66.8, 80.6, 125.2, 126.6.

4-Methyl-1-oxaspiro[4.5]dec-7-ene (61). Mixture of diastereoisomers: yield 0.41 g (80%); oven temperature 120 °C (15 Torr); IR (film) 1457, 1436, 1177, 1096 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 1.00 (3 H, d, J = 6.24 Hz), 1.30–2.46 (9 H, complex absorption), 3.86 (2 H, m), 5.69 (2 H, m). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.74; H, 10.49.

4,8-Dimethyl-1-oxaspiro[4.5]dec-7-ene (62).[10] Mixture of diastereoisomers: yield 0.10 g (71%); oven temperature 96 °C (15 Torr) (lit.[10] bp 83 °C (11 Torr)).

4,7,8-Trimethyl-1-oxaspiro[4.5]dec-7-ene (63). Mixture of diastereoisomers: yield 0.25 g (78%); oven temperature 135 °C (10 Torr); IR (film) 1128, 1050, 1023 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 0.96 (3 H, d, J = 6.4 Hz), 1.63 (6 H, s), 1.76–2.36 (9 H, complex absorption), 3.8 (2 H, m). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.09; H, 11.12.

1-Oxaspiro[4.5]decane (64):[5,8a] yield 0.26 g (88%); oven temperature 70 °C (15 Torr) (lit.[5] bp 72–75 °C (19 Torr); lit.[8a] bp 52 °C (8 Torr)).

8-Methyl-1-oxaspiro[4.5]decane (65).[10] Mixture of diastereoisomers: yield 0.19 g (67%); oven temperature 78–80 °C (15 Torr) (lit.[10] bp 79 °C (18 Torr)).

4-Methyl-1-oxaspiro[4.5]decane (66). Mixture of diastereoisomers: yield 0.13 g (85%); oven temperature 110–115 °C (10 Torr); IR (film) 1149, 1074, 1040 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 0.97 (3 H, d, J = 6.94 Hz), 1.11–2.32 (13 H, complex absorption), 3.80 (2 H, m). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.82; H, 12.09.

4,8-Dimethyl-1-oxaspiro[4.5]decane (67).[10] Mixture of diastereoisomers: yield 0.10 g (92%); oven temperature 95 °C (15 Torr) (lit.[10] 91 °C (15 Torr)).

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Intramolecular Addition Reactions of Carbonyl Ylides Formed during Photocyclization of Aryl Vinyl Ethers

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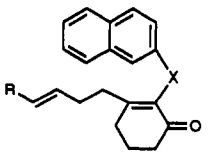
Photocyclization of aryl vinyl ethers reportedly proceeds via carbonyl ylide intermediates. The photochemical behavior of several aryl vinyl ethers, which incorporate a pendant alkene side chain, was explored. Naphthyl vinyl ethers **1c** and **1d** provided products that are consistent with photocyclization and subsequent intramolecular ylide–alkene addition. Product distribution is influenced by solvent and temperature effects. Thus, irradiation of **1c** in toluene provides **9a** in 87% yield. However, irradiation of **1c** in methanol/toluene (1:1) provides **3c** (45%), **11** (24%), and **12** (23%). Product **12** results from photoinitiated intramolecular [2 + 2] cycloaddition of the butenoate ester side chain to the naphthalene system.

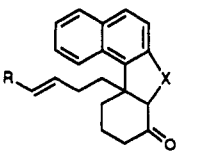
Introduction

Photocyclization of aryl vinyl ethers reportedly proceeds via a six-electron rearrangement to provide carbonyl ylide intermediates. In the absence of other effects these systems rearrange by a process involving hydrogen shifts to provide dihydrofuran products.[1,2] Although the literature is abundant with examples of carbonyl ylide cycloadditions, surprisingly little use has been made of the aryl vinyl ether photolysis for preparation of these 1,3-dipoles.[3] Usual methods for the generation of the carbonyl ylide species have involved thermolysis and photolysis of oxirane rings,[4] carbene addition to carbonyl groups,[5] and extrusion reactions such as the thermolysis of oxadiazolines.[6] We report here some preliminary results on the intramolecular addition reactions of carbonyl ylides, which are generated on photolysis of aryl vinyl ethers.

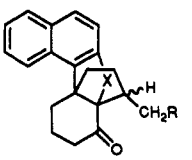
Recently, we reported that aryl vinyl sulfides bearing a pendant alkene side chain undergo photocyclization and subsequent intramolecular ylide–alkene addition.[7-9] Significant structure and temperature effects have been noted for the photocyclization–intramolecular addition of aryl vinyl sulfides. It is of interest therefore to compare the products of these reactions with those from the aryl vinyl ether photolyses described below. In summary, photolysis of **1a** with Pyrex-filtered light favors formation of hydrogen shift product **2a** at low temperatures (–78 °C to room temperature) and intramolecular addition product **3a** at high temperature (110 °C). Conversely, photolysis of **1b** provides **3b** as the major product regardless of the temperature employed (–78 to 110 °C).[10]



1a, X = S, R = H
b, X = S, R = CO_2Et
c, X = O, R = CO_2Et
d, X = O, R = H



2a, X = S, R = H
b, X = O, R = CO_2Et
c, X = O, R = H



3a, X = S, R = H
b, X = S, R = CO_2Et
c, X = O, R = CO_2Et
d, X = O, R = H

Results and Discussion

Aryl vinyl ether **1c** was prepared from 3-ethoxycyclohexenone via the epoxide **6a** as shown. Photolysis of a

(1) For reviews see: Schultz, A. G. *Acc. Chem. Res.* **1983**, *16*, 210. Schultz, A. G.; Motyka, L. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 1.

(2) Wolff, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6157. Wolff, T. *J. Org. Chem.* **1981**, *46*, 978.

(3) (a) For a recent review of 1,3-dipolar cycloaddition chemistry, see: *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley Interscience: New York, 1984; Vol. 1–2. (b) For a review of intramolecular dipolar cycloaddition reactions, see: Padwa, A. In *New Synthetic Methods*; Verlag Chemie: New York, 1979; Vol. 5, pp 25–69. (c) *Advances in Cycloaddition*; Curran, D. P., Ed.; Jai Press: Greenwich, CT, 1988; Vol. 1.

(4) Eberbach, W.; Brokatzky, J.; Fritz, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 47. Eberbach, W.; Brokatzky, J. *Tetrahedron Lett.* **1980**, 4909. Trossolo, A. M.; Leslie; T. M.; Sarpotdar, A. S., Small, R. D.; Ferraudi, G. J. *Pure Appl. Chem.* **1979**, *51*, 261. Clawson, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 153 and 159.

(5) Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100. Padwa, A.; Hornbuckle, S. F.; Fryxell, G. E.; Stull, P. D. *J. Org. Chem.* **1989**, *54*, 817.

(6) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 4260.

(7) Dittami, J. P.; Ramanathan, H.; Breining, S. *Tetrahedron Lett.* **1989**, *30*, 795.

(8) Dittami, J. P.; Nie, X.-Y. *Synth. Commun.* **1990**, *20*(4), 541.

(9) Dittami, J. P.; Nie, X.-Y.; Buntel, C.; Rigatti, S. *Tetrahedron Lett.* **1990**, 3821.

0022-3263/91/1956-5572$02.50/0