(not shown) are obtained using the lower field signal. The parent compounds **6a-9a** generally give a poor fit, and this is consistent with the small, but measureable, permanent dipoles recorded (**8a** and **9a**, μ = 0.4 and 1.0 D respectively)[3] for the molecules and the fact that this is not recognized by the zero value of the Hammett substituent constant for H. The most sensitive centers to substituent effects are the exocyclic olefinic carbons. As the electron-donating capacity of the remote para substituent increases, the electron density at C1 and the centers adjacent to the ring fusion is enhanced and the centers are shielded. Although the more remote positions (**6** and **8**: C2a/C6a; C7 and C9; C3/C4) are also influenced, the effect is smaller (Figure 2, Tables I-III). Because the electron density of the exocyclic double bond is directed toward C1 the influence of the electron-rich para substituent upon the arylmethylene center (C8/C6) is notably the opposite to that for C1, and a deshielding effect is recorded. This is in precisely the opposite direction to shifts recorded for C1 of *p,p'*-disubstituted 1,1-diarylethenes. In DMSO-d_6 C1 of 1,1-diphenylethene resonates at δ 149.2 but the *p,p'*-dimethoxy, dimethylamino, and trimethylammonio derivatives have this same signal at 148.2, 149.0, and 145.4 ppm, respectively. However, as Sardella and co-workers[20] have shown, the effect of a remote aryl substituent upon the exocyclic olefinic centers of 6-aryl-6-methylfulvene is primarily due to π-polarization because of a marked (~70°) twist angle of the aryl ring to the flat cyclopentadienylidene moiety. This results in a π-electron excess or deficiency at the C1' ipso-center as a result of the C4' substituent. An attenuation of the resonance effect is involved, and the dominance of π-polarization accounts for the major changes in the exocyclic olefinic resonances and the reversal in slope of the fulvene C6 correlation. A similar effect is likely in **8** and **9** since **8c** has a twist angle for the aryl substituent of 28° in the solid state.[21] The situation in **6** and **7** is less obvious as the twist angle of the aryl substituent is only 5° in **6c**. It appears therefore that the cyclopropparenyl moieties of **6-9** either behave as electron acceptors or donate *less* π-electron density when electron donors are located at the remote para positions. It is notable that the nitro substituted compounds **6e** and **8e** provide chemical shift data which match expectations from the plots of Figure 2. These serve to support the ambiphilicity of the cyclopropparenyl moiety.

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5-Methylene-2(5*H*)-furanone as a Dienophile in Diels-Alder Cycloadditions: Site Selectivity and Regioselectivity

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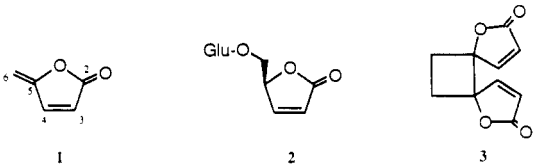
Site selectivity and regioselectivity in Diels-Alder reactions of 5-methylene-2(5*H*)-furanone (**1**) with several acyclic dienes have been investigated. We have found that **1** consistently reacts specifically at the exocyclic double bond, giving spiro adducts in good yields. Excellent regioselectivity has also been found in either catalyzed or uncatalyzed reactions with unsymmetrically substituted dienes. A kinetic study of the reaction with isoprene has revealed that the observed regioselectivity is a direct consequence of kinetic control over the process. Theoretical calculations have been carried out in order to interpret these experimental results.

The blistering property and antibiotic activity of many plants belonging to the natural order Ranunculaceae are well-known.[1] These physiological activities are attributable to protoanemonin (**1**), an α,β-unsaturated lactone that is released in the plant upon crushing of the tissues with enzymatic splitting of the glucoside ranunculin (**2**).[2-5] Protoanemonin easily dimerizes through a [2 + 2] head-to-head cycloaddition to anemonin (**3**), the crystalline product normally isolated from Ranunulaceae.

Chart I



1 **2** **3**

Although **1** is easily prepared from levulinic acid,[6] its potential reactivity as a multifunctional C_5 synthon has scarcely been explored, and few explanations have been advanced for its physiological activity.[7] Its electrophilic

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(2) Hill, R.; van Heyningen, R. *Biochem. J.* **1951**, *49*, 332.
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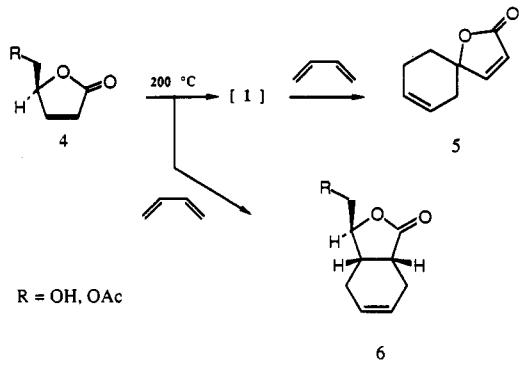
0022-3263/90/1955-3060$02.50/0

Scheme I



behavior toward a variety of nucleophiles has been studied. However, since these reactions usually give a complex mixture of products, no immediate synthetic utility could be found.[8]

We now report that protoanemonin displays general reactivity as a dienophile in Diels–Alder cycloadditions. Since it has two different double bonds with a complicated system of activation (it is a conjugated lactone but also an enol lactone), cycloaddition could, in principle, afford several products. However, as we have found very recently, **1** reacts specifically at the exocyclic double bond with butadiene, forming the spiro adduct **5**.[9] This compound was previously observed as a byproduct in the reaction of lactones **4**. At that time, we showed that it came from **1** by elimination of water (or acetic acid) under the drastic conditions of the reaction (Scheme I).

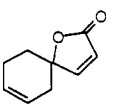
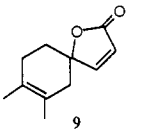
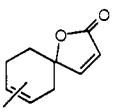
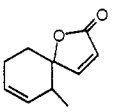
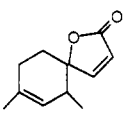
The special olfactive properties of the spiro lactone **5** and the synthetic usefulness of similar lactones[10] led us to begin a systematic study of this serendipitous finding. Two major areas were targeted: the exocyclic double bond reactivity (site selectivity), and regioselectivity when asymmetrically substituted dienes are used. The experimental results were interpreted in light of theoretical calculations carried out at the same time.

Results and Discussion

1. Site Selectivity. Reaction of 5-methylene-2(5*H*)-furanone (**1**) with butadiene (**7**), 2,3-dimethylbutadiene (**8**), 2-methyl-1,3-butadiene (isoprene) (**10**), (*E*)-1,3-pentadiene (*trans*-piperylene) (**12**), and (*E*)-2-methyl-1,3-pentadiene (**14**) at ca. 150 °C for 4 h afforded adducts **5**, **9**, **11**, **13**, and **15**, respectively, in good yields (see Table I). These spirolactones were the sole isolated reaction products; compounds arising from the endocyclic double bond acting as dienophile were never detected. It is interesting to note that **1** reacts faster (lower temperature, shorter reaction time) than butenolides **4** (R = OR′, SR′, H, etc.), which require 20 h at 200 °C to afford similar yields of Diels–Alder adducts **6** (Scheme I).[11]

Lactones **9**, **11**, **13**, and **15** have not been described previously in the literature, and their structures were assigned on the basis of their spectroscopic data. Characteristic infrared carbonyl absorption at 1750 cm^{-1} and ^1H NMR chemical shifts for the lactone olefinic protons at δ 5.8–6.2 and 7.2–7.6 were observed in all cases. Moreover, ^{13}C NMR spectra confirmed the spiro ring juncture of these compounds, showing the quanternary carbon atom signal at 80–90 ppm. The two regioisomers of adduct **11** were separated by column chromatography, the major product being identified as the para isomer by ^{13}C NMR spectral correlations. In the reactions of dienes **12** and **14** only regioisomers **13** and **15** were formed; these assignments were made on the basis of their NMR spectral data, and GLC showed the presence (90:10) of the two possible diastereoisomers in each case. Compounds **5**, **9**, **11**, **13**, and **15** are good precursors for a variety of substances with interesting olfactive properties,[12] making the cycloaddition reaction of **1** with dienes reported herein a convenient and general entry to these kinds of aromas.[13]

Table I. Diels–Alder Reactions of Protoanemonin (1) with Dienes

diene	temp,[a] °C	% yield[b]	adduct
 7	155	85	 5
 8	170	81	 9
 10	155	77	 11
 12	150	64	 13
 14	150	75	 15

[a] Reaction time was 4 h. [b] Isolated yields.

Table II. Energies (eV) of Frontier Orbitals of Dienes and 1

compd	HOMO	LUMO
butadiene	−9.352	0.462
2,3-dimethylbutadiene	−9.058	0.505
isoprene	−9.214	0.496
trans-piperylene	−9.056	0.442
2-methyl-1,3-pentadiene	−8.961	0.474
1	−9.957	−0.984

Table III. Coefficients of the LUMO of 1 on Carbon Atoms

C_2	C_3	C_4	C_5	C_6
−0.308	−0.498	0.539	0.259	−0.467

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(13) Details on the preparation and synthetic applications of adducts will be published elsewhere.

Theoretical calculations using the AM1 method[14] were carried out in order to interpret this site selectivity. Table II shows the energies of the frontier orbitals of butadiene, isoprene, *trans*-piperylene, 2,3-dimethylbutadiene, 2-methyl-1,3-pentadiene, and protoanemonin. It can be seen that in all cases the energy difference between the HOMO of the diene and the LUMO of protoanemonin is smaller than the energy gap for the reversed frontier orbitals. Therefore, the reactions of these dienes with the dienophile **1** can be classified as a normal Diels–Alder cycloaddition.[15]

Nevertheless, frontier orbital theory[16] fails to predict the site selectivity. Thus, examination of the protoanemonin LUMO coefficients for the carbon atoms involved in the formation of the new bonds predicts a preferential participation of the endocyclic C–C double bond, in contrast with the experimental results. Table III shows that the LUMO coefficients of the 3–4 bond are larger than the LUMO coefficients of the 5–6 bond.

The failure of the frontier orbital theory in the prediction of the observed site selectivity has previously been found in other Diels–Alder cycloadditions,[17] and it indicates that factors other than these orbital terms play an important role in the process. Although Diels–Alder reactions are generally thought to be concerted, there is probably a considerable amount of biradical character in the transition states, particularly for reactions involving unsymmetrical dienes and dienophiles. Thus, it seems reasonable to assume that any interpretation of the site selectivity must take into account this biradicaloid nature of the transition structures.

Dannenberg and Franck[18] have suggested that the stability of such hypothetical biradical structures can be estimated in similar cases by calculating the relative energies of the species resulting from the attack of a hydrogen atom at the different possible sites which could be involved in the formation of the first bond. In our case, optimization of the geometry of the radicals corresponding to the bonding of an additional hydrogen atom to either C_3 or C_6 of **1** indicates that the latter should be more favorable by 2.7 kcal/mol. This result indicates that the attack of butadiene at the C_6 position of **1** to give the exocyclic adduct would be preferred in a hypothetical biradical mechanism.

The relative stabilities of these radicals can be understood in terms of a simple qualitative argument based on π-electron delocalization. In fact, protoanemonin presents three conjugated double bonds: if H attacks at C_6, the radical formed is stabilized by extended conjugation through the endocyclic double bond and the carbonyl group, while in an initial attack at C_3, the overall conjugation disappears and the radical is only stabilized as in allylic systems. Furthermore, the radical obtained by the attack at C_6 is further stabilized in light of the captodative theory as enunciated by Viehe.[19]

In addition to the described electronic effects which aid in explaining the observed experimental facts, there are steric effects which can also be invoked. In point of fact, the formation of the exocyclic adduct involves attack at a terminal methylene, while in the endocyclic TS, the first bond formed is on a ring olefinic atom.

Table IV. Uncatalyzed and $AlCl_3$-Catalyzed Reactions of 1 with Isoprene

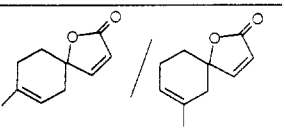
temp, °C	time, h	equiv of $AlCl_3$	% yield	 11p/11m
25	21	0.33	38	26
25	21	1	38	24.6
25	140	0.33	39	24.0
63	120		24	20.7
95	48		52	12.2
108	3		69	9.8
118	1		64	8.9
130	0.75		68	8.2
140	0.4		58	7.5
155	4		77	5.6

Table V. Experimental Pseudo-First-Order Rate Constants[a] (k_{obs}/s^{-1}) for the Formation of Para (k_p) and Meta (k_m) Regioisomers from Protoanemonin and Isoprene

temp, °C	$10^5\ k_p$	$10^5\ k_m$
108	9.61 ± 0.01	0.98 ± 0.01
118	17.1 ± 0.06	1.91 ± 0.06
140	51.6 ± 0.08	6.86 ± 0.08

[a] 90% confidence limit.

2. Regioselectivity. 5-Methylene-2(5*H*)-furanone (**1**) was allowed to react with isoprene (**10**), *trans*-piperylene (**12**), and (*E*)-2-methyl-1,3-pentadiene (**14**) in order to study the regioselectivity of the cycloaddition. The effects of temperature and catalysts on the regioselectivity were also investigated.

The reaction of **1** with isoprene was performed under different conditions, as shown in Table IV. In all cases two regioisomers, **11*p*** and **11*m***, were obtained. The ratio **11*p*/11*m*** was found to be temperature dependent and varied from 21:1 to 6:1 over a temperature range from 63 to 155 °C. Regioselectivity was not substantially increased by the use of $AlCl_3$ as catalyst, the ratio of para/meta isomers remaining independent of the dienophile–catalyst molar proportion. In all catalyzed experiments, the total yields of adducts were lower than in the uncatalyzed cycloadditions due to partial polymerization of **1** induced by the presence of the strong Lewis acid under the reaction conditions.

A kinetic study of the uncatalyzed cycloaddition was conducted at temperatures of 108, 118, and 140 °C. The rate constants for each regioisomer are shown in Table V. (See Experimental Section). The energy barriers for the formation of both regioisomers were determined from plots of ln [para] and ln [meta] vs $1/T$, respectively. The obtained values were $E_p = 16.3 \pm 0.3$ kcal/mol and $E_m = 18.9 \pm 0.6$ kcal/mol, with an energy gap of 2.6 kcal/mol. These activation energies show that the predominant formation of the para isomer can be explained in terms of a kinetically controlled process.

Regioselectivity is even more important in the reactions of protoanemonin with *trans*-piperylene (**12**) and (*E*)-2-methyl-1,3-pentadiene (**14**). These compounds, which both bear a methyl in the extreme of the dienic system, afford only one regioisomer in each case, that in which this methyl is found in the ortho position (Table I).

In order to explain these facts, electronic factors can again be invoked and analyzed through the Dannenberg–Franck treatment mentioned above. Thus, attack of a hydrogen atom at the C_1 atom of isoprene leads to a radical

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1.9 kcal/mol more stable than the radical resulting from attack at the C_4 position, explaining the predominant formation of the para adduct in the reaction of isoprene with **1**. In a similar way, this radical stability criterion favors the experimentally observed adduct by 6.1 and 7.6 kcal/mol in the reactions of *trans*-piperylene and (*E*)-2-methyl-1,3-pentadiene, respectively, with **1**. These great energy differences explain why the second regioisomer is not experimentally observed.

Conclusions

5-Methylene-2(5*H*)-furanone (**1**) has proven to be a good dienophile in Diels–Alder cycloaddition reactions with acyclic dienes. A very marked site selectivity has been observed in all cases, leading to the exclusive formation of spirolactones, via participation of the exocyclic C–C double bond of **1**.

Excellent regioselectivity has also been found in cycloaddition reactions involving unsymmetrically substituted dienes bearing the substituent on the carbon atoms involved in the formation of the new σ bonds (e.g., *trans*-piperylene or 2-methyl-1,3-pentadiene). Whereas in these cases only one regioisomer was obtained, reaction with isoprene afforded two regioisomers whose distribution was temperature dependent. A kinetic study of the cycloaddition to isoprene indicated that the observed regioselectivity is a direct consequence of kinetic control over the process. Theoretical calculations show that the experimental facts are consistent with a biradicaloid structure in the transition states and indicate that both steric and electronic factors play important roles in the site and regioselectivities of these reactions.

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 Procedure for Theoretical Calculations. The AM1 method[14] was used in the energy calculation. Total geometry optimization was performed throughout. Calculations were performed at the restricted open Hartree–Fock (ROHF) level of theory in the case of radicals. All calculations were carried out with the AMPAC program[20] using the VAX 8800 and the HP 9000/8355 computer systems.

General Experimental Procedures. (a) Uncatalyzed Reactions. Reactions or protoanemonin (**1**) with dienes **7**, **10**, **12**, and **14** were effected at 150–155 °C, and the reaction with diene **8** was carried out at 170 °C (Table I) for 4 h. These reactions were conducted in sealed tubes containing 1 mmol of dienophile, 45 mmol of the freshly distilled diene, and a trace of hydroquinone. The adducts were purified by column chromatography on silica gel, using mixtures of hexane–ethyl acetate as eluents. The major diastereoisomers of adducts **13** and **15** were thus isolated. The kinetic study of the cycloaddition between protoanemonin and isoprene was performed by using sealed tubes containing the reactants. The reaction was carried out in a thermostated bath which was heated to the desired temperature (108, 118, and 140 ± 0.5 °C) (Table V). At intervals three tubes were cooled, opened, concentrated, and analyzed by gas chromatography. The proportion of para/meta isomers was determined from the ratio of peak areas using naphthalene as internal standard. The response factors of each adduct and the starting lactone **1** were obtained vs the internal standard through calibration curves. The operation was carried out at five time intervals.

(b) Catalyzed Reactions. A typical experiment was run as follows: A mixture of protoanemonin (419 mg, 4.3 mmol) and sublimated aluminum chloride (194 mg, 1.4 mmol) in dry dichloromethane (5 mL) was stirred for 45 min. Then freshly distilled isoprene (10 mL) was added. After 21 h of stirring at room temperature, aqueous sodium bicarbonate (50 mL) was added and the mixture was extracted with dichloromethane. The organic extracts were dried (Na_2SO_4), and the solvent and excess isoprene as well as unreacted protoanemonin were removed at reduced pressure. The residue was filtered on silica gel (hexane–ethyl acetate) to afford 273 mg (38% yield) of **11*p*/11*m*** adducts in a 26:1 ratio. Chromatography allowed the isolation of the major regioisomer **11*p***.

1-Oxaspiro[4.5]deca-3,7-dien-2-one (5): 250 mg, 85% yield; mp 65–66 °C (lit.[21] mp 66–67 °C); IR (KBr) 1758, 1654, 1603 cm^{-1}; MS, *m/e* (relative intensity) 150 (M, 5.0), 68 (24.6), 54 (100.0); 400-MHz ^1H NMR 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 δ 22.9, 30.7, 33.6, 86.5, 120.2, 122.4, 126.2, 159.3, 171.8.

7,8-Dimethyl-1-oxaspiro[4.5]deca-3,7-dien-2-one (9): 25.5 g, 81% yield; oven temperature 85–90 °C (0.02 Torr); IR (KBr) 1760, 1602 cm^{-1}; MS, *m/e* (relative intensity) 179 (M + 1, 7.1), 178 (M, 7.9), 82 (80.1), 68 (15.2), 67 (100.0), 55 (18.0), 54 (50.7), 53 (21.9), 51 (18.3), 43 (19.1); 400-MHz ^1H NMR δ 1.60 (3 H, s), 1.64 (3 H, s), 1.73 (1 H, m), 1.85 (1 H, m), 2.00–2.35 (4 H, complex absorption), 6.00 (1 H, d, J = 5.56 Hz), 7.42 (1 H, d, J = 5.56 Hz); 20-MHz ^{13}C NMR δ 17.8, 17.9, 28.5, 30.6, 39.0, 86.8, 119.4, 120.9, 124.5, 159.5, 171.4. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.16; H, 8.12.

8-Methyl-1-oxaspiro[4.5]deca-3,7-dien-2-one (11*p*): 33.3 g, 65% yield; oven temperature 84 °C (0.1 Torr); IR (film) 1750, 1605 cm^{-1}; MS, *m/e* (relative intensity) 165 (M + 1, 29.2), 164 (M, 39.1), 149 (34.1), 97 (21.5), 92 (26.0), 91 (22.6), 82 (24.9), 79 (29.3), 77 (29.2), 69 (22.4), 68 (100.0), 67 (98.4), 65 (22.2), 55 (25.7), 54 (53.6), 53 (46.5), 52 (15.2), 51 (22.7), 41 (22.2); 80-MHz ^1H NMR δ 1.70 (3 H, br s), 1.9 (2 H, m), 2.2 (2 H, m), 5.35 (1 H, br s), 6.02 (1 H, d, J = 5.30 Hz), 7.48 (1 H, d, J = 5.30 Hz); 20-MHz ^{13}C NMR δ 23.1, 28.0, 31.3, 34.1, 86.9, 116.9, 120.5, 133.8, 159.9, 172.3. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.94; H, 7.44.

6-Methyl-1-oxaspiro[4.5]deca-3,7-dien-2-one (13): 225 mg, 64% yield. The major diastereoisomer is described: oven temperature 90–95 °C (0.04 Torr); IR ($CHCl_3$) 1755, 1650, 1600 cm^{-1}; MS, *m/e* (relative intensity) 165 (M + 1, 1.5), 164 (M, 3.0), 68 (100.0), 93 (26.5), 41 (37.6); 80-MHz ^1H NMR δ 0.86 (3 H, d, J = 7.30 Hz), 1.67–2.50 (4 H, complex absorption), 2.7 (1 H, m), 5.40–5.90 (2 H, complex absorption), 6.1 (1 H, d, J = 5.90 Hz), 7.4 (1 H, d, J = 5.90 Hz); 20-MHz ^{13}C NMR δ 15.6, 24.5, 31.6, 37.3, 90.3, 121.8, 125.4, 130.0, 157.5, 172.0. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.68; H, 7.66.

6,8-Dimethyl-1-oxaspiro[4.5]deca-3,7-dien-2-one (15): 20 g, 70% yield. The major diastereoisomer is described: oven temperature 95–100 °C (0.02 Torr); IR (film), 1760, 1600 cm^{-1}; MS, *m/e* (relative intensity) 179 (M + 1, 1.7), 178 (M, 3.4), 82 (100.0), 67 (77.3), 54 (27.4), 41 (32.9); 80-MHz ^1H NMR δ 0.85 (3 H, d, J = 7.30 Hz), 1.73 (3 H, br s), 1.83–2.33 (4 H, complex absorption), 2.70 (1 H, m), 5.23 (1 H, br s), 6.12 (1 H, d, J = 6.00 Hz), 7.47 (1 H, d, J = 6.00 Hz); 20-MHz ^{13}C NMR δ 15.9, 22.6, 29.2, 31.8, 37.5, 90.5, 121.7, 124.6, 132.8, 157.6, 172.0. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.11; H, 8.03.

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