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DIELS-ALDER CYCLOADDITIONS OF CHIRAL BUTENOLIDES WITH BUTADIENE AND ISOPRENE: DIASTEREOFACIAL SELECTIVITY AND REGIOSELECTIVITY

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Abstract.- Chiral butenolides react with butadiene at 210° giving optically active bicyclic compounds with excellent diastereoselectivity, in good yields. Optical purity of the adducts has been verified either by chemical correlation and/or by the use of $Eu(hfc)_3$. Reactions with isoprene at 125-220° afford 1:1 mixtures of regioisomers, selectivity being increased by the use of $AlCl_3$ as catalyst, at lower temperatures.

INTRODUCTION

α,β-Unsaturated carbonyl compounds have been widely used in Diels-Alder cycloadditions. Thus, many examples exist in the literature about the behaviour of acrylic acid derivatives,[1] and unsaturated ketones[2] as dienophiles. However, α,β-butenolides (2(5H)-furanones) have been scarcely exploited.[3-8]

Chiral α,β-butenolides are useful synthons in the preparation of natural products[9] due to their density of chemical functions conferring them a great versatility. On the other hand, the Diels-Alder reaction is one of the most powerful methods utilized in asymmetric synthesis.[1] Combination of these two features must allow the access to more complicated skeletons containing many chiral centers, and to accomplish this synthetic purpose stereo- and regioselectivity of the cycloaddition must be governed.

We report in this paper the Diels-Alder reactions of several enantiomerically pure 5-substituted-2(5H)-furanones with butadiene and isoprene, focussing the attention in the syn/anti facial selectivity and the regioselectivity.

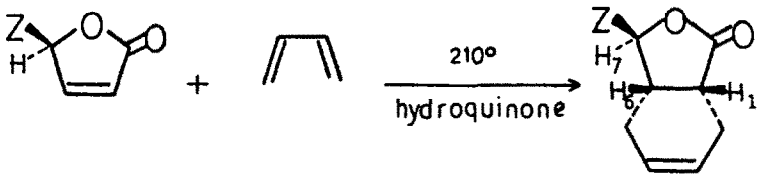
RESULTS AND DISCUSSION

a) Reactions with butadiene.[10]

Our investigations started with the study of the reactions between butenolides 1-8 and butadiene (Scheme 1 and Table 1). Compounds 2-8 were prepared from D-ribonolactone,[8,11,12] and chosen as representative chiral 2(5H)-furanones having substituents at C-5 position that differ in size and polarity. Achiral crotonolactone 1 was used as an easily available model [13] to probe the best reaction conditions.

Thus, reaction of butenolides with excess butadiene, at 210° for 20 hours, in the presence

of hydroquinone, afforded bicycloadducts 9-16 in good yields (Table 1). When lactones 4 and 5 were used as dienophiles the expected adducts were obtained in lower yield due to elimination processes (H_2O, AcOH) in the pyrolytic conditions, that lead to the formation of byproducts.



Scheme 1

Table 1. Reactions of several butenolides with butadiene

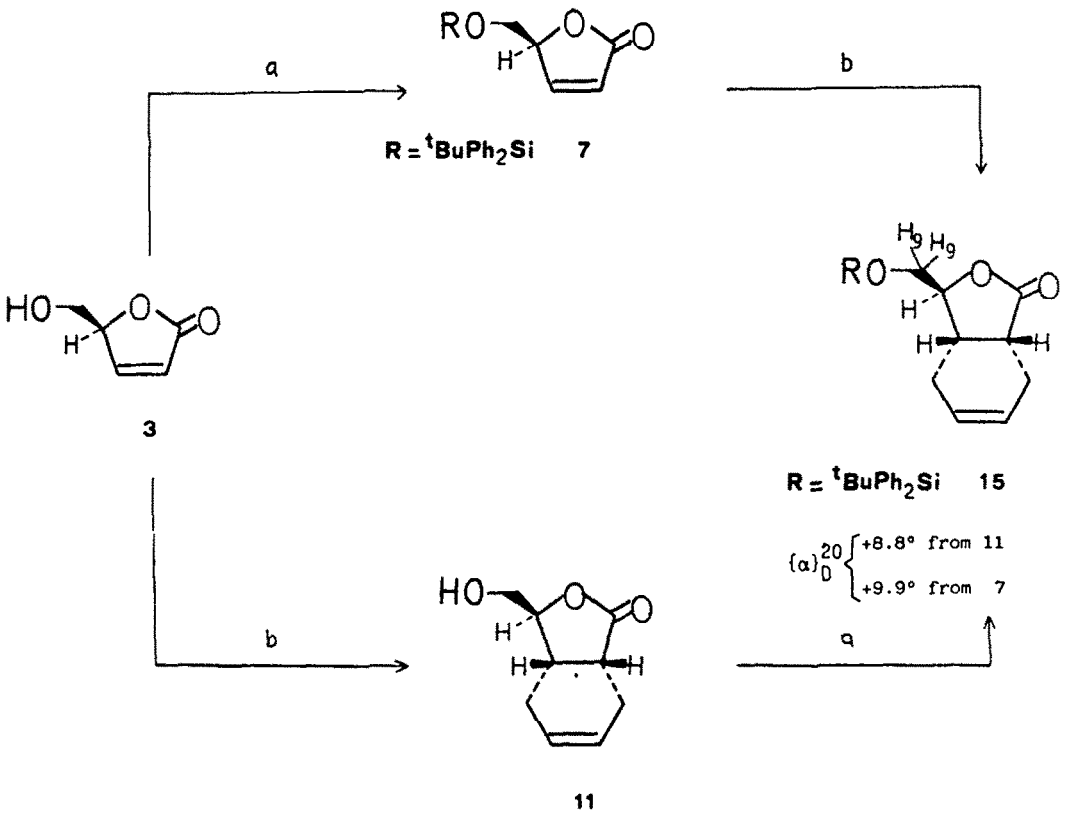
Entry	Z	Butenolide[+]	Adduct	% Yield
(1)	H	1[13]	9	62
(2)	CH_3	2[12]	10	63
(3)	CH_2OH	3[11]	11	32
(4)	CH_2OAc	4[11]	12	53
(5)	CH_2OMe	5[11]	13	77
(6)	CH_2OBn	6[11]	14	80
(7)	$CH_2OSiPh_2{}^tBu$	7[8]	15	90
(8)	CH_2SPh	8[12]	16	66

[+]Formulae are displayed in Scheme 1.

Anti facial selectivity was always observed since only single diastereoisomeric adducts were obtained (HPLC, cmr), even when the Z substituent in the dienophile was not a bulky group, as in the case of lactones 2-5. The stereochemistry of the adducts was determined from their pmr spectra and is governed by preferential interaction of butadiene with the less hindered side of the conjugate double bond of the butenolides in the TS. Indeed, in adducts 10-16 the coupling constants $J_{6,7}$ (Scheme 1) are ∿4 Hz and this value agrees with a trans relationship[14] for these protons showing the attack of butadiene to the (3re,4si)-face, giving (1R,6S)-adducts.

This selectivity is much better than that observed in uncatalyzed cycloadditions between several dienes and open chain acrylic acid derivatives[1] and substituted cyclohexenones,[2] that give mixtures of diastereoisomers. Much effort has been done in order to rationalize the diastereofacial selectivity in Diels-Alder cycloadditions involving chiral dienophiles. Thus, steric effects have been invoked to exert control over the facial selectivity,[15] and when an allylic substitution with heteroatom functionality is present on a dienophile, rules based on electrostatic considerations have been formulated to assign facial stereochemistry.[16] In our case, molecules having a conjugated double bond contained in a five membered lactone ring, both steric and electrostatic arguments are consistent with the observed selectivity.

Optical purity of bicyclic adducts 10-16 was established either by chemical correlation and/or by the use of the chiral shift reagent tris|3-heptafluorobutiryl-d-camphorato|europium(III), $Eu(hfc)_3$. Scheme 2 shows the correlation of products 3, 7, 11, and 15, from which enantiomeric purity of adducts 11 and 15 was verified. Thus, the known[11] hydroxymethylbutenolide 3, was made to react with $Ph_2{}^tBuSiCl$ and 4-(dimethylamino)pyridine in dichloromethane at 0° for 30 min, giving the lactone 7, $[\alpha]_D^{20}$ = -77.6° (c 6.26, $CHCl_3$) (lit[8] $[\alpha]_D^{24}$ = -81.8°, c 10.5, $CHCl_3$). Increasing the reaction time resulted in a partial racemization of 7. Cycloaddition of this compound with butadiene afforded the adduct 15, $[\alpha]_D^{20}$ = +9.9° (c 4.1, $CHCl_3$). On the other hand, cycloaddition reaction of butenolide 3 and butadiene gave the hydroxyadduct 11, $[\alpha]_D^{20}$ = -6.5 (c 2.9, $CHCl_3$), that by reaction with $Ph_2{}^tBuSiCl$ as described above for compound 3 yielded 15, $[\alpha]_D^{20}$ = +8.8 (c



a: $^tBuPh_2SiCl$, DMAP, 0°C; b: butadiene, 210°C.

Scheme 2

4.5, $CHCl_3$). It is noteworthy the good agreement of the optical rotation values for product 15,[8] synthesized by these two alternative ways. Moreover, the 400 MHz pmr spectrum of pure 15, obtained by route b/a (Scheme 2), in the presence of 0.5 eq of $Eu(hfc)_3$ showed only one set of signals, while the absorption peaks corresponding to one of the methylene protons at C-9 position (Scheme 2), at δ3.94-3.99, appear clearly duplicated for the partially racemic adduct 15.[17] (Fig 1). Therefore, all these experiments prove that compound 15 (Scheme 2, route b/a) is optically pure, and so is hydroxyadduct 11.

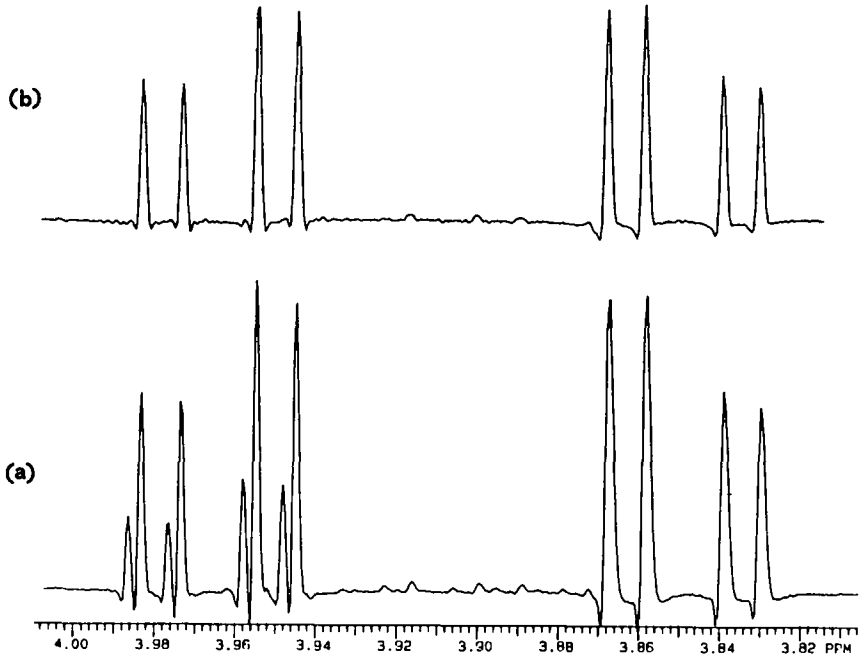


Fig. 1. 400 MHz pmr absorption peaks for the two methylene protons H_9 of 15. (a) Partially racemized compound. (b) Pure enantiomer.

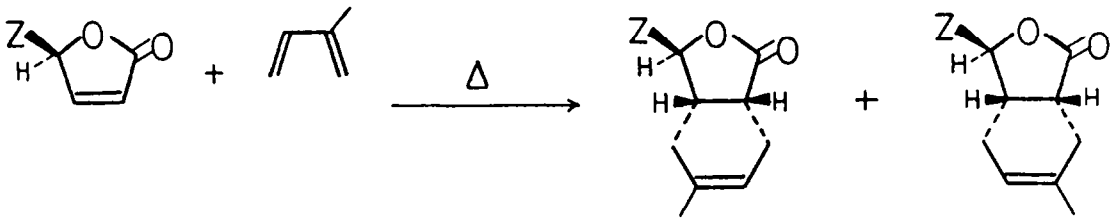
The other adducts were tested in a simmilar manner by comparison of the chiral lanthanide shiftedspectra of products obtained from enantiomerically pure and from racemic[17] butenolides, respectively. For instance, Fig 2 shows the 80 MHz pmr spectrum of 10, obtained from β-angelica lactone 2 and butadiene, recorded in absence of chiral shift reagent and the spectra of both the racemic[18] and the single enantiomeric forms in the presence of 0.6 eq of $Eu(hfc)_3$.

b) Reactions with isoprene.[19]

Uncatalyzed reactions of lactones 2 and 6 with excess isoprene as solvent, at 185-220° for 20 hours afforded 19a/b and 20a/b, respectively, as a 1:1 mixture of para/meta regioisomers, in good yields (Scheme 3, Table 2 entries 2-4). The same equimolecular mixture 20a/b was produced when butenolide 6 reacted with isoprene at 125° C, (entry 1) but in this case the yield in adducts was only 22%. Thus, the reaction temperature seems to have no influence on the regioselectivity.[20]

The presence of a/b regioisomers of 19 and 20 was detected by analytical HPLC and capillary GC, and confirmed by 400 MHz pmr (all absorption peaks appeared duplicated), but no separation was possible.

Complete anti facial selectivity in these cycloadditions was evidenced by the trans relationship found between the Z group and the cyclohexene moiety in all adducts 19 and 20, as deduced from the fairly constant value (4 Hz) of the coupling constants $J_{6,7}$, that requires a trans arrangement for these protons, by analogy with the cycloadducts obtained from these same butenolides and butadiene, described above.



Z = Me 2 19a 19b

CH_2OBn 6 20a 20b

Scheme 3

Table 2. Reactions of butenolides 2 and 6 with isoprene

Entry	Butenolide	Eq isoprene	Eq $AlCl_3$	Solvent	Temperature (°C)	Time	% Yield	a/b ratio[++]
(1)	6	excess	---	---	125	20 h	22	50 / 50
(2)	2	excess	---	---	185	20 h	57	50 / 50
(3)	2	excess	---	---	200	20 h	80	50 / 50
(4)	6	excess	---	---	220	20 h	52	50 / 50
(5)	2	excess	0.33	---	30	6 d	30	80 / 20
(6)	2	excess	0.33	---	50	48 h	42	80 / 20
(7)	2	excess	0.33	---	50	6 d	57	80 / 20
(8)	2	excess	1.0	---	50	48 h	11	83 / 17
(9)	2	23	0.33	CH_2Cl_2	50	48 h	47	83 / 17
(10)	2	23	0.33	CH_2Cl_2	50	6 d	84	85 / 15

[+] Yield calculated on the unrecovered starting material, except in entries 1-4.

[++] Determined by capillary GC.

The use of $AlCl_3$ as catalyst resulted in a remarkable para regioselectivity in the cycloaddition. The role of temperature, amount of catalyst and diene, and reaction time was investigated in order to maximize regioselectivity, while keeping good yields, and some selected experiments are shown on Table 2. The optimal conditions found consisted in treatment of lactone 2, chosen as a model, with 23 eq of isoprene and 0.33 eq of $AlCl_3$ in dichloromethane as solvent at 50° for six days, affording 19a/b as a 85:15 mixture, in 84% yield (Table 2, entry 10). The major isomer was assumed to be 19a, as deduced from the calculated frontier orbital coefficients of these reactants in a normal Diels-Alder cycloadditions,[21] and also considering the experimental results on catalyzed cycloadditions of acrylic acid derivatives with isoprene.[22]

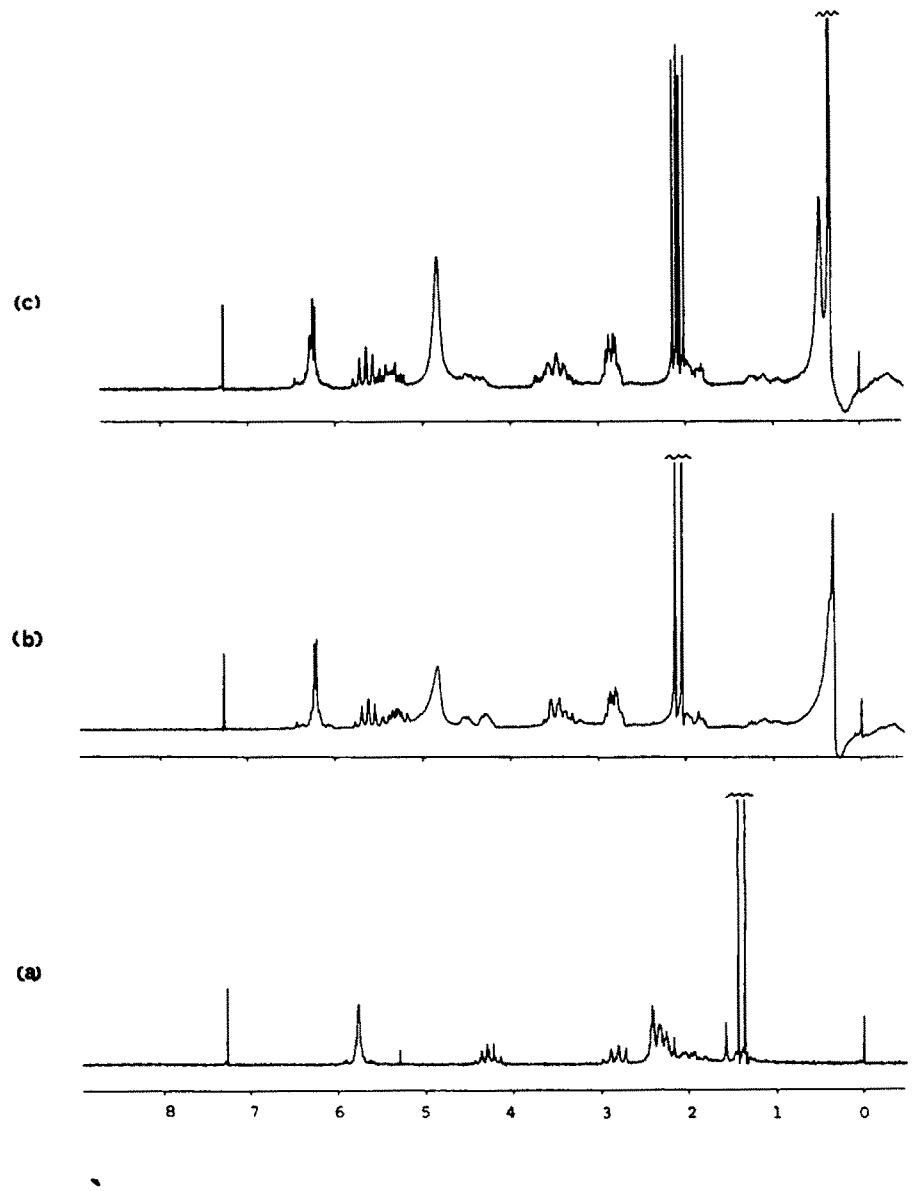


Fig. 2. 80 MHz pmr spectra for adduct 10. (a) In the absence of chiral shift reagent. (b) In the presence of 0.6 eq of $Eu(hfc)_3$, pure enantiomer. (c) Same as (b), racemic compound.

CONCLUSION

From the results reported herein we can conclude that chiral α,β-butenolides react with butadiene to give adducts in good yields, with excellent diastereofacial selectivity while optical purity remains unaltered. On the other hand, acceptable regioselectivity is obtained in the catalyzed reaction of these dienophiles with isoprene. Synthetic applications of the bicyclic adducts are under investigation.

EXPERIMENTAL SECTION

Melting points have been determined on a Kofler hot stage and are uncorrected. Optical rotations were obtained on a Propol polarimeter, model Dr. Kernchen. Distillation of small amounts were effected on a rotational distillator Büchi, model KRV 65/30 (only external or oven temperature given). The 70 eV electron impact mass spectra were recorded on a Perkin-Elmer spectrometer, model 1310. The 80 MHz pmr and 20 MHz cmr spectra were recorded on a Bruker spectrometer model WP 80 SY, from chloroform-d solutions, unless otherwise indicated; the 400 MHz pmr spectrum of compound 15 was recorded on a Varian spectrometer, model VXR 400; chemical shifts are given in parts per million relative to TMS (δ scale). Microanalyses were performed at the Instituto de Química Bio-Orgánica, C.S.I.C., Barcelona.

(S)-5-Diphenyl-t-butylsiloxymethyl-2(5H)-furanone, 7. To a solution of 3 (300 mg, 2.6 mmol) and 4-(dimethylamino)pyridine (960 mg, 7.9 mmol) in methylene chloride (25 ml) diphenyl-t-butylsilyl chloride (1.37 ml, 5.3 mmol) was added. After stirring for 30 min at 0°C under argon atmosphere, the reaction mixture was diluted with methylene chloride and washed with 1% hydrochloric acid, and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel to afford butenolide 7 (750 mg) in 81% yield; m.p. 78.5-79.5°C; $[\alpha]_D^{20}$ -77.6° (c 6.3, in chloroform) (lit[8] m.p. 79-80°C; $[\alpha]_D^{24}$ -81.8 (c 10.5, in chloroform)); ir (chloroform) 1770, 1605, 1485, 1445 cm^{-1}; pmr 3.04 (s, 9H); 3.89 (d, J 4.8 Hz, 2H); 5.04 (m, 1H); 6.16 (dd, J 5.8 Hz, J' 1.9 Hz, 1H); 7.28-7.72 (complex abs, 11 H); cmr 18.89, 26.45, 63.07, 82.97, 122.25, 127.56, 129.68, 132.33, 132.54, 135.21, 153.69, 172.39; ms, m/e 353 (M+1, 1), 295 (65.9), 237 (21.6), 189 (15.1), 181 (21.5), 139 (18.0), 135 (24.9), 115 (23.4), 105 (35.4), 91 (16.9), 55 (100.0), 41 (28.7).

Diels-Alder cycloadditions of butenolides and butadiene. A typical experiment was run as follows: Butadiene (15 ml) was bubbled in a reactor containing butenolide 2 (250 mg, 2.5 mmol) and a trace of hydroquinone, cooled in an acetone-dry ice bath. The reactor was stoppered and heated at 210°C in a silicone bath for 24 hours. After cooling the mixture was washed with acetone and the solvent and excess butadiene were removed to give a residue that was cromatographed on silica gel (mixtures of hexane-ethyl acetate as eluents) to afford 243 mg of adduct 10 (63% yield). Multigramme scale preparations were performed on an Autoclave Burton Corblin, model Zipperclave 500, tested at 225 bar pressure. Yields were essentialy identical (50-60%) as when using glass tubing reactors.

Physical and spectral characteristics of the adducts are the following:

8-Oxabicyclo|4.3.0|non-3-en-9-one, 9.[23]

B.p. 70°/0.1 torr; ir (film) 1770, 1660 cm^{-1}; pmr 1.53-2.95 (complex abs, 6H); 4.01 (dd, J 9.4 Hz, J' 2.0 Hz, 1H); 4.31 (dd, J 9.4 Hz, J' 5.0 Hz, 1H); 5.75 (broad s, 2H); cmr 21.89, 24.57, 31.88, 37.12, 72.62, 124.79, 125.02, 178.94; ms, m/e 138 (M, 47.8), 105 (42.4), 97 (45.6), 93 (51.5), 91 (52.1), 80 (22.7), 79 (100.0), 78 (18.1), 77 (83.4), 68 (17.5), 65 (16.2), 53 (18.2), 51 (23.8).

(1R,6S,7R)-7-Methyl-8-oxabicyclo|4.3.0|non-3-en-9-one, 10.[3]

B.p. 90°/0.08 torr; $[\alpha]_D^{20}$ -25.6° (c 1.5, in chloroform); ir (film) 1760, 1650 cm^{-1}; pmr 1.41 (d, J 6.15, 3H); 1.64-2.55 (complex abs, 5H); 2.83 (m, 1H); 4.29 (dq, J 6.1 Hz, J' 4.3 Hz, 1H); 5.75 (broad s, 2H); cmr 18.99, 21.98, 24.19, 36.43, 38.81, 80.77, 124.91, 125.35, 178.70; ms, m/e 152 (M, 8), 137 (9.9), 107 (33.9), 105 (37.0), 91 (28.8), 83 (17.4), 80 (30.5), 79 (100.0), 77 (50.0), 69 (22.3), 55 (18.7), 51 (19.7), 43 (37.7), 41 (32.1).

(1R,6S,7S)-7-Hydroxymethyl-8-oxabicyclo|4.3.0|non-3-en-9-one, 11.

B.p. 160°/0.035 torr; $[\alpha]_D^{20}$ -6.5° (c 2.9, in chloroform); ir (film) 3700-3100, 1770, 1660 cm^{-1}; pmr 1.57-3.28 (complex abs, 7H); 3.80 (ABX, J_{AB} 13.3 Hz, J_{AX} 5.1 Hz, J_{BX} 3.8 Hz, 2H); 4.20 (dt, J 5.1 Hz, J' 3.8 Hz, 1H); 5.79 (broad s, 2H); cmr 23.30, 24.77, 33.58, 37.41, 62.81, 85.33, 125.47, 126.04, 179.69; ms, m/e 168 (M, 8.2), 150 (1.2), 137 (22.7), 91 (22.9), 80 (16.7), 79 (100.0), 78 (30.9), 77 (35.5). Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.00; H, 7.46.

(1R,6S,7S)-7-Acetoxymethyl-8-oxabicyclo|4.3.0|non-3-en-9-one, 12.

B.p. 120°/0.05; $[\alpha]_D^{20}$ +6.8° (c 2.0, in chloroform); ir 1770, 1735, 1650 cm^{-1}; pmr 1.53-3.06 (complex abs, 6H); 2.11 (s, 3H); 4.04-4.46 (complex abs, 3H); 5.84 (broad s, 2H); cmr 20.37, 22.15, 24.59, 34.15, 36.73, 63.94, 81.54, 125.11, 125.90, 170.14, 178.24; ms, m/e 210 (M, 8.0), 168 (17.6), 150 (31.6), 149(31.5), 137 (31.2), 105 (52.9), 104 (39.6), 103 (19.1), 91 (29.6), 81 (21.2), 80 (24.1), 79 (100.0), 78 (39.0), 77 (35.0), 43 (51.1). Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.96; H, 7.05.

(1R,6S,7S)-7-Methoxymethyl-8-oxabiciclo|4.3.0|non-3-en-9-one, 13.

B.p. 110°/0.04 torr; $[\alpha]_D^{20}$ +2.60° (c 2.4 in chloroform); ir 1775 cm^{-1}; pmr 1.57-3.09 (complex abs, 6H); 3.38 (s, 3H); 3.58 (d, J 4.4 Hz, 2H); 4.22 (q, J 4.4 Hz, 1H); 5.80 (broad s, 2H); cmr 22.35, 25.68, 34.41, 37.07, 59.40, 73.12, 83.52, 125.38, 126.13, 179.20; ms, m/e 182 (M,

3.7), 150 (2.7), 137 (26.7), 105 (34.1), 91 (20.6), 81 (15.8), 79 (100.0), 78 (15.9), 77 (24.9), 45 (20.7). Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.78; H, 8.08.

(1R,6S,7S)-7-Benzyloxymethyl-8-oxabicyclo|4.3.0|non-3-en-9-one, **14.**

B.p. 160°/0.05 torr; $[\alpha]_D^{20}$ +5.66 (c 1.7, in chloroform); ir 1770, 1655, 1595, 1480, 1450 cm^{-1}; pmr 1.55-3.14 (complex abs, 6H); 3.68 (d, J 3.9 Hz, 2H); 4.24 (q, J 3.9 Hz, 1H); 4.57 (s, 2H); 5.82 (broad s, 2H); 7.32 (s, 5H); cmr 22.12, 25.04, 34.15, 36.83, 70.37, 73.29, 83.34, 125.22, 125.82, 127.26, 127.45, 128.12, 137.49, 178.88; ms, m/e 258 (M, 0.8), 107 (27.5), 91 (100.0), 81 (15.8), 79 (87.8), 77 (22.1), 65 (21.2). Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.26; H, 7.24.

(1R,6S,7S)-7-Diphenyl-t-butylsiloxymethyl-8-oxabicyclo|4.3.0|non-3-en-9-one, **15.**[8]

M.p. 63-65°; $[\alpha]_D^{20}$ +9.9 (c 4.12, in chloroform) (lit.[8] m.p. 73-74°; $[\alpha]_D^{24}$ +19.6° (c 10, in chloroform)); ir (chloroform) 1765, 1590, 1475, 1430 cm^{-1}; pmr (400 MHz) 1.05 (s, 9H); 1.90 (m, 1H); 2.21-2.46 (complex abs, 3H); 2.7 (m, 1H); 3.00 (dt, J 7.2 Hz, J' 4.4 Hz, 1H); 3.75 and 3.86 (ABX, J_{AB} 11.2 Hz, J_{AX} 4.0 Hz, J_{BX} 3.6 Hz, 2H); 4.16 (deceptive q, J 3.6-4.0 Hz, 1H); 5.75-5.87 (complex abs, 2H); 7.45 (m, 6H); 7.70 (m, 4H); cmr 19.10, 22.48, 25.43, 26.74, 34.07, 37.37, 64.32, 84.82, 125.60, 126.35, 127.77, 129.85, 132.64, 132.89, 135.44, 135.51, 179.30.

(1R,6S,7S)-7-Phenylthiomethyl-8-oxabicyclo|4.3.0|non-3-en-9-one, **16.**

B.p.175°/0.04 torr; $[\alpha]_D^{20}$ -0.20° (c 1.97, in chloroform); ir 1770, 1665, 1580, 1480, 1435 cm^{-1}; pmr 1.51-3.00 (complex abs, 6H); 3.04 and 3.30 (ABX, J_{AB} 13.9 Hz, J_{AX} 7.6 Hz, J_{BX} 5.1 Hz, 2H); 4.23 (ddd, J 7.6 Hz, J' 5.1 Hz, J" 3.8 Hz, 1H); 5.78 (broad s, 2H); 7.09-7.52 (complex abs, 5H); cmr 22.16, 25.27, 36.05, 36.51, 36.98, 82.84, 125.21, 125.86, 126.78, 129.02, 130.02, 134.80, 178.10; ms, m/e 260 (M, 60.9), 123 (27.9), 110 (23.2), 109 (25.3), 105 (19.6), 91 (24.1), 81 (24.7), 79 (100.0), 77 (49.9), 65 (18.7), 51 (16.6), 45 (19.1).
Anal. Calcd. for $C_{15}H_{16}O_2S$: C, 69.22; H, 6.20; S, 12.29. Found: C, 68.96; H, 6.39; S, 11.80.

Preparation of adduct **15** from **11**. To a solution of hydroxyadduct **11** (110 mg, 0.59 mmol) and 4-(dimethylamino)pyridine (215 mg, 1.78 mmol) in methylene chloride (10 ml) diphenyl-t-butylsilyl chloride (0.31 ml, 1.19 mmol) was added and the mixture was stirred for 4.5 h at 0° under argon atmosphere. The reaction mixture was diluted with methylene chloride, washed with 1% hydrochloric acid and dried over anhydrous sodium sulfate. After evaporation of the solvent, the formed silanol was removed by distillation at 100°/0.005 torr to give a residue that was chromatographed on silica gel (hexane-ethyl acetate as eluent) to afford compound **15** (227 mg, 86% yield); $[\alpha]_D^{20}$ +8.8 (c 4.54, in chloroform).

Diels-Alder cycloadditions of butenolides and isoprene.

(a) Uncatalyzed reactions. The procedure was simmilar to that described above for the reactions of butenolides and butadiene.
(b) Catalyzed reactions. A typycal experiment was run as follows: To a stirred suspension of aluminium chloride (135 mg, 1.01 mmol) in dry methylene chloride (4 ml) a solution of -angelica lactone, **2**, (347 mg, 3.54 mmol) in dry methylene chloride (8 ml) was added. Then, isoprene (7.1 ml) was added and the resultant solution was heated at 50-55° for 6 days. The reaction mixture was poured into sat aqueous calcium bicarbonate (25 ml) at 0° and extracted with methylene chloride (2x20 ml), and dried over anhydrous sodium sulfate. The solvent was removed and the residue was chromatographed on silica gel (mixtures of ether-hexane as eluents) to afford 222 mg of **19a/b** as a 85:15 mixture and 144 mg of **2** (84% yield on the unrecovered starting material).

Physical and spectral characteristicas of adducts **19** and **20**, as a 50:50 a/b mixtures are the following:

(1R,6S,7R)-(3,7-Dimethyl- and 4,7-dimethyl)-8-oxabicyclo|4.3.0|non-3-en-9-one, **19b/a.**

70-75°/0.03 torr; ir (film) 1790 cm^{-1}; pmr 1.39 (d, J 6.7 Hz) and 1.40 (d, J 6.7 Hz) (3H); 1.70 (s, 3H); 2.1 (m, 5H); 2.75 (dt, J 8 Hz, J' 7.5 Hz, 1H); 4.25 (dq, J 6.2 Hz, J' 5 Hz, 1H); 5.43 (m, 1H); ms, m/e 166 (M, 21.8), 93 (100.0). Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.50. Found: C, 71.99; H, 8.71.

(1R,6S,7S)-(3-Methyl- and 4-methyl)-7-benzyloxymethyl-8-oxabicyclo|4.3.0|non-3-en-9-one, **20b/a.**

85-90°/0.03 torr; ir (film) 1760, 1600, 1580, 1490, 1450 cm^{-1}; pmr (400 MHz) 1.65 (s) and 1.66 (s) (3H); 1.85 (m, 2H); 2.20 (m, 2H); 2.56 (m) and 2.62 (m) (1H); 2.89 (m) and 2.97 (m) (1H); 3.60 and 3.64 (ABX, 2H); 4.17 (m, 1H); 4.52 (m, 2H); 5.51 (m) and 5.54 (m) (1H); 7.28 (complex abs, 5H); ms, m/e 272 (M, 10), 91 (100). Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.65; H, 7.54.

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