SYNTHESIS OF 1,1-BIS(3,5-DIMETHYL-2-FURYL)ETHENE; THE CHEMO- AND SITE-SELECTIVITY OF ITS CYCLOADDITIONS

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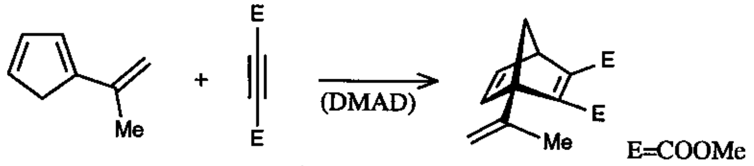
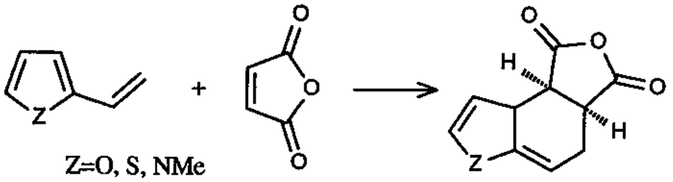
Abstract - The new polyene 1,1-bis(3,5-dimethyl-2-furyl)ethene (**11**) was derived from 2,4-dimethylfuran. Its reaction with dienophiles such as maleic anhydride, benzoquinone or 1-cyanovinyl acetate generated exclusively Diels-Alder adducts (9-oxabicyclo[4.3.0]nona-1,7-diene derivatives) involving the exocyclic double bond and one double bond of one furyl unit. The reaction of **11** with didehydrobenzene (benzyne) gave a 7-oxabicyclo[2.2.1]hepta-2,5-diene derivative resulting from the exclusive Diels-Alder addition of one furyl group, whereas dimethyl acetylenedicarboxylate added to **11** giving a mixture of the corresponding 7-oxabicyclo[2.2.1]hepta-2,5-diene and 9-oxabicyclo[4.3.0]nona-1,4,7-triene derivatives. With allenic acid, **11** added in a [2+2] fashion exclusively with its exocyclic double bond giving 2-[3,3-bis(3,5-dimethyl-2-furyl)cyclobutylidene]acetic acid with high selectivity.

The cycloadditions of 1- and 2-vinylcyclopentadiene to strong dienophiles have been shown to involve primarily the cyclopentadiene moiety (see e.g. eq. (1)).[1] In contrast the Diels-Alder reactions of vinylheterocyclodienes such as 2-vinylfurans,[2] 2-vinylthiophenes,[3] 2-vinyl-*N*-alkylpyrroles[4] (see e.g. eq. (2)) or 3-methyl-5-vinylisoxazole[5] (eq. (3)) give preferentially adducts involving the exocyclic double bond.

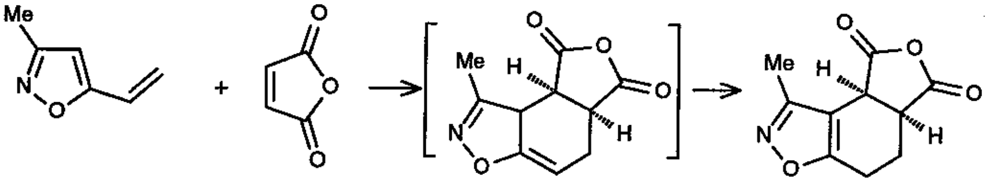
Similarly, methyl propynoate adds to 2-vinylfuran (**1**) after prolonged heating to 80°C and gives a low yield (2%) of the dehydrogenated adduct (**2**) together with polymeric material.[2] In contrast, dimethyl acetylenedicarboxylate (DMAD) adds to **1** already at 20°C and leads to a 1:1 mixture (10%) of the 7-oxanorbornadiene derivative (**3**) and the benzofuran (**4**). At 80°C, adduct **3** is not observed.[2] As for **1**, the



eq. (1)

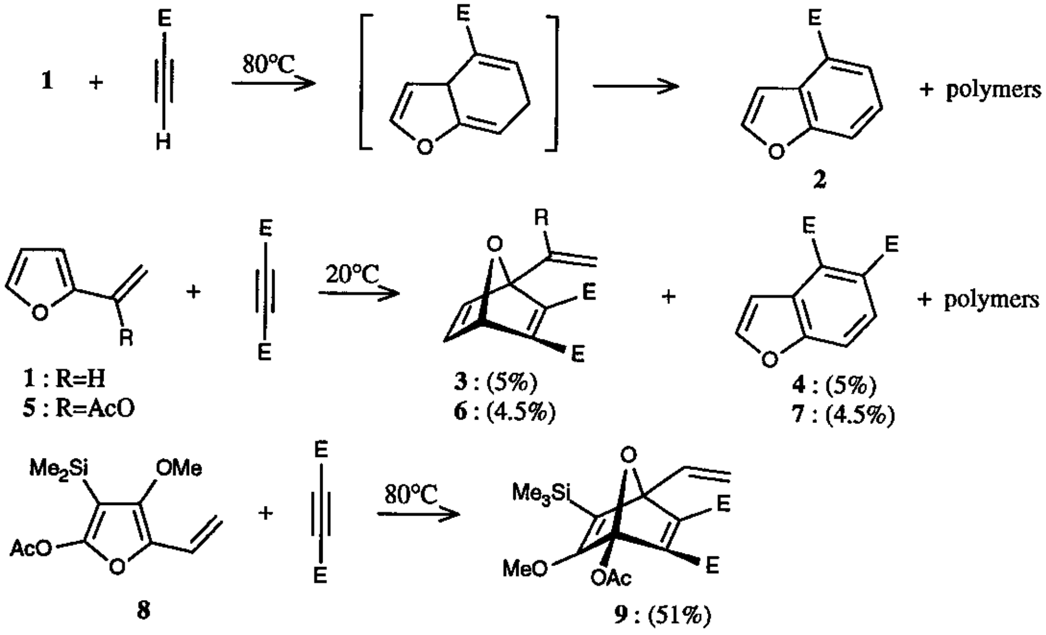


eq. (2)



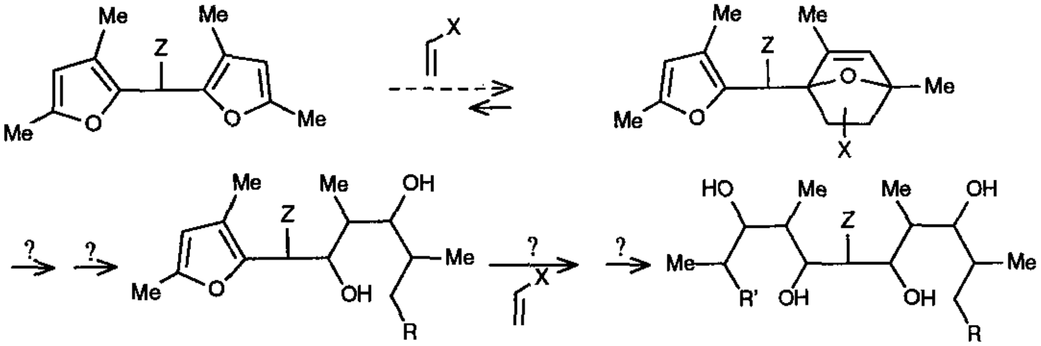
eq. (3)

reaction of DMAD with the 1-(α-furyl)vinyl acetate (**5**) gave a 1:1 mixture (9%) of products (**6**) and (**7**), together with polymeric material.[2] With the persubstituted furan derivative (**8**), the reaction with DMAD furnishes the corresponding 7-oxanorbornadiene system (**9**) in reasonable yield (51%).[6] These results suggest that the site-selectivity of the Diels-Alder additions of 2-vinylfurans depends on the type of substitution of the furan ring and on the nature of the dienophile.



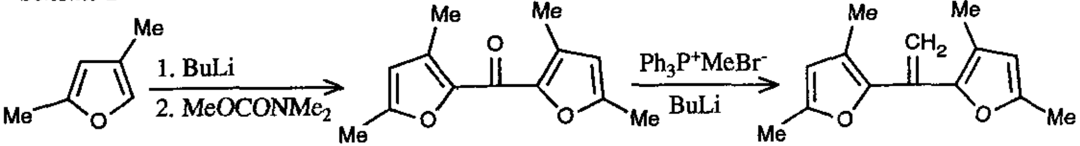
The 7-oxabicyclo[2.2.1]heptenyl derivatives have proved to be quite valuable starting materials for the synthesis of natural products or compounds of biological interest.[7,8] With the goal in mind to develop a new approach to the synthesis of polypropionate fragments (acylic chain with contiguous carbon centers substituted alternatively with methyl and hydroxy groups) intervening in a large number of antibiotics[9] according to *Scheme 1*, we have prepared 1,1-bis(3,5-dimethyl-2-furyl)ethene (**11**) from 2,4-dimethylfuran[10,11] and have explored its reactivity toward a number of dienophiles. Our preliminary results reported here show that as in the case of 2-vinylfurans and depending on the nature of the dienophile Diels-Alder addition involving exclusively one of the furan moiety can compete with [4+2]-cycloadditions involving the exocyclic double bond. We show also that thermal [2+2]-cycloadditions involving exclusively the ethene moiety can also compete.

Scheme 1



Treatment of 3,5-dimethylfuran[10,11] with 1 equivalent of BuLi generated the corresponding 2-furyllithium derivative the reaction of which with methyl *N,N*-dimethylcarbamate provided ketone (**10**) in 61% yield. Wittig condensation of **10** with methylidenetriphenylphosphorane gave 1,1-bis(3,5-dimethyl-2-furyl)ethene (**11**: 90%), a compound undergoing polymerization at room temperature (*Scheme 2*). A 1:1 mixture of **11** and maleic anhydride in ether led to the formation (20°C, 3 days) of a single Diels-Alder adduct (**12**), isolated in 80% yield. Nuclear Overhäuser Effect (NOE) measurements between the angular methyl group signal at δ_H = 1.36 ppm and the vicinal proton at C(2)) of the 7-oxabicyclo[4.3.0]nona-5,8-diene moiety (δ_H = 3.50 ppm) in

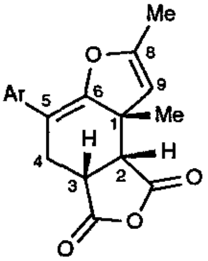
Scheme 2



10 **11**

the ^{1}H-nmr spectrum confirmed the structure of **12**. The comparison of the uv absorption spectra of **11** (λ_{max} = 257 nm (ε = 3500), 281 (6100)) and **12** (λ_{max} = 280 nm (ε = 13200)) suggested only a small change between **11** and **12** in terms of π overlap between the furyl and olefinic chromophores (see below).

Similarly, **11** added to benzoquinone (20°C, 3 d) giving a single adduct (**13**) (80% conversion) whose isolation was problematic due to its instability and concurrent polymerization. The ^{1}H-nmr spectrum (NOE measurements) of the crude reaction mixture allowed one, however, to establish the structure of **13**. As in the case of **12**, the *endo* selectivity (Alder rule[12]) was followed. The reaction of a 1:1 of **11** and 1-cyanovinyl acetate (20°C, 10 d) led to a *ca.* 6:1 mixture of adducts (**14**) (27%) and (**15**) (5%) separated by flash chromatography on silica gel. The cycloaddition was highly regioselective and site-selective since no trace of any other isomeric adduct could be detected in the ^{1}H-nmr spectrum of the crude reaction mixture. Double irradiation experiments in the ^{1}H-nmr spectra of **14** and **15** did not allow one to establish unambiguously the relative configuration of their centres C(2).



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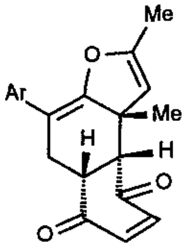

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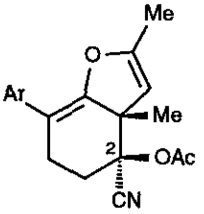

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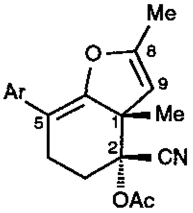

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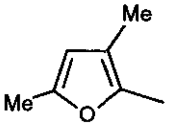
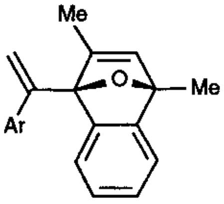
Ar = 

Contrary to the Diels-Alder additions of **11** with maleic anhydride, benzoquinone and 1-cyanovinyl acetate which gave exclusively 7-oxabicyclo[4.3.0]nona-5,8-diene derivatives involving the ethylene moiety of **11** and one endocyclic double bond of one of the dimethylfuryl ring, the reaction of **11** with benzyne generated by decomposition of anthranilic acid with isopentyl nitrite[13] gave a low yield (10%) of a single adduct (**16**) resulting from the Diels-Alder addition of one furyl ring as diene. No adduct involving the exocyclic double bond of **11** could be detected in the ^{1}H-nmr spectrum of the crude reaction mixture. The low yield of this reaction can be attributed to the fast polymerization of **11** under the conditions used to engender benzyne.[13] In some assays, the benzoic acid derivative (**17**) was isolated as by-product in low yield (2-7%). This product arises probably from the electrophilic substitution of one hydrogen atom of the ethene moiety of **11** by

2-oxycarbonylphenyl cation intermediate generated by decomposition of ortho-benzenediazonium-carboxylate.



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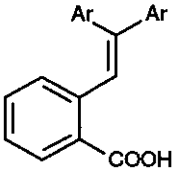

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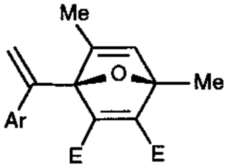

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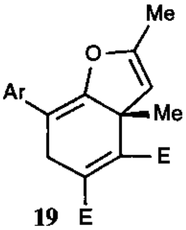
+



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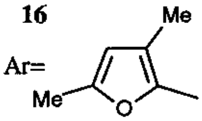
Ar=



E=COOMe

Interestingly, dimethyl acetylenedicarboxylate (DMAD) added to **11** (1:1 mixture, no solvent, 20°C, 3 d) giving a 1:4 mixture of the Diels-Alder adducts (**18**) and (**19**), separated and isolated by column chromatography on silica gel in 12% and 48% yield, respectively. No trace of a double adduct resulting from the reaction of the two dimethylfuryl moieties could be seen in the ^{1}H-nmr spectrum of the crude reaction mixture. The structures of **17** - **19** were readily deduced from their spectral data. While the uv absorption of **19** (λ_{max}= 276 nm (ε = 13700)) was very similar to those of **12** - **15**, that of **18** (λ_{max} = 240 (ε = 10700), 343 (12150)) indicated an enhancement of the π overlap between the remaining dimethylfuryl ring and the exocyclic double bond.

Table: Product ratio **18** /**19** and rate constants for the Diels-Alder addition **11** + DMAD under various conditions (1:1 mixture of **11** and DMAD, 20 °C)

solvent	neat	MeCN	CH_2Cl_2	PhH	PhH/Et_3Al[a)]
concentration [mol/dm^3]	2.9	0.12	0.11	0.16	0.11
reaction time [days]	3	12	12	12	1 hour
conversion rate	88%	86%	83%	60%	b)
18 /**19**	1:4	1:2.4	1:2.5	1:4	1:6
rate constant $k \cdot 10^5$[mol^{-1}s^{-1}]		4.8±0.15	4.7±0.08	1.0±0.15	b)

a) 1 equivalent of Et_3Al, 20°C

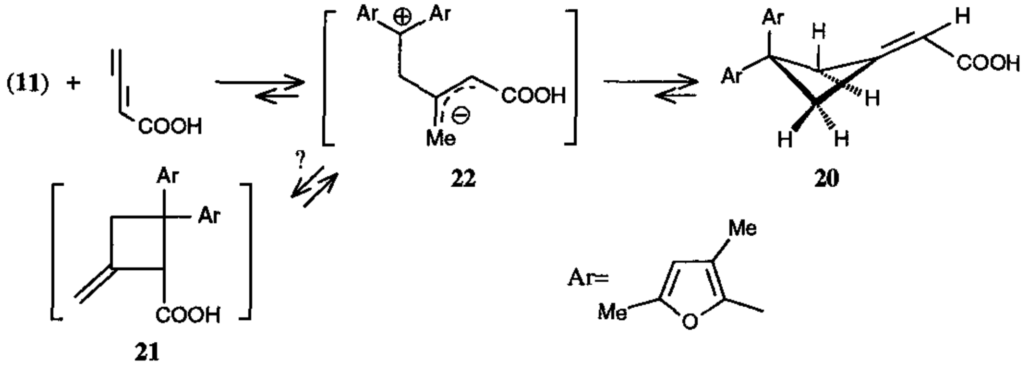
b) polymerization was important.

In order to increase the proportion of the 7-oxanorbornadiene product (**18**), we studied the effect of solvent and of Lewis acid catalysts on the cycloaddition **11** + DMAD (see Table). The best adduct ratio **18**/**19** = 1:2.4 was realized for the reaction in MeCN. Nearly the same product ratio was observed in CH_2Cl_2, a significantly less polar solvent than MeCN. In benzene, the product ratio was not better than when **11** and DMAD were allowed to react without solvent. Most Lewis acid catalysts such as $AlCl_3$, ZnI_2, or $BF_3 \cdot Et_2O$ led to quick polymerization of **11**. Nevertheless, with $AlEt_3$, the cycloaddition of **11** to DMAD was concurrent with the polymerization of **11**, leading to a 1:6 mixture of **18** and **19** in very low yield. Apparently, under Lewis acid-catalyzed conditions there is no improvement of the proportion of **18** with respect to **19**. At this stage it is clear that the Diels-Alder additions of **11** are not a suitable mean to approach polypropionate fragment synthesis as suggested on *Scheme 1*.

Adducts **18** and **19** were stable under prolonged heating in boiling $CHCl_3$ or toluene. Attempts to equilibrate these compounds at higher temperature all failed. In boiling DMSO, **18** produced an orange polymer while **19** gave a black mixture of polymerized materials. Our kinetic data (Table) show a slight solvent effect on the rate of the cycloadditions **11** + DMAD, the reaction being faster in the more polar solvents MeCN and CH_2Cl_2 than in benzene. Parallel with these results, the proportion of the 7-oxanorbornadiene derivative **18** increases with the solvent polarity. Nevertheless, the observed effects are relatively small, suggesting concerted Diels-Alder additions[14] with transition states sharing little zwitterionic character.[15]

Allenic dienophiles are known to add to furan and derivatives giving 7-oxanorbornene systems.[16] To our surprise, when **11** was allowed to react with one equivalent of buta-2,3-dienoic acid in ether (20°C, 3 d), one single product (**20**) was formed (^1H-nmr of the crude reaction mixture) together with concurrent polymerization of **11**. Adduct (**20**) resulted from a [2+2]-cycloaddition involving exclusively the exocyclic double bond of **11**. Its structure was deduced readily from its spectral data (including NOE measurements in the ^1H-nmr spectrum) which were consistent only with a symmetrical structure or a mixture of two rapidly equilibrating species leading to equivalent 3,5-dimethyl-2-furyl substituents. The isomeric adduct (**21**) could not be seen in the ^1H-nmr spectra of the crude reaction mixture. This result was expected for a [2+2]-cycloaddition involving an electron-rich olefin such as **11** and an allene substituted with an electron-withdrawing group.[17] For reasons of gauche interactions between the furyl and carboxylic group in **21**, this compound is expected to be less stable than **20**. By analogy with other [2+2]-cycloadditions of allene derivatives, the reaction **11** + $CH_2{=}C{=}CHCOOH$ follows probably a non-concerted, two-step mechanism[18] involving the zwitterionic intermediate (**22**) (*Scheme 3*).[19]

Scheme 3



The uv absorption spectrum of **20** (λ_{max} = 220 nm (ε = 16500), 286 (2020)) is similar to that of **11**, except for the band at 220 nm typical of the β,β-dialkyl acrylic acid chromophore.[20] This observation confirms that there is little π conjugation between the 3',5'-dimethyl-2'-furyl and ethylene moieties in **11** - **16** and **19** (see above), the furyl rings being nearly perpendicular to the olefinic systems due to steric effects. Rotation about the C(1)-C(2') bonds in **11** is not completely prohibited as the Diels-Alder additions with maleic anhydride, benzoquinone and 1-cyanovinyl acetate gave exclusively adducts involving both the exocyclic double bond and one double bond of one of the two furyl moieties. The site- and chemoselectivity of the reaction of **11** with various dienophiles may thus be controlled in part by the torsional barrier about its C(1)-(2') bonds.

Not unexpectedly, ketone (**10**) did not react with any of the dienophiles used in this study.

Conclusion

Depending on the nature of the dienophile, 1,1-bis(3,5-dimethyl-2-furyl)ethene (**11**) can undergo either a Diels-Alder addition involving exclusively one of its furyl moiety, or a Diels-Alder addition involving one double bond of one furyl system and the ethylene double bond, or a [2+2]-cycloaddition involving exclusively the exocyclic double bond. The cycloadditions can be highly stereoselective (*endo*-Alder rule) and regioselective.

ACKNOWLEDGMENTS

We are grateful to *F. Hoffmann-La Roche & Co.*, AG (Basel), the *Fonds Herbette* (Lausanne) and the *Swiss National Science Foundation* (bourse dans le cadre du renforcement de la coopération avec les Etats de l'Europe de l'Est) for financial support.

EXPERIMENTAL PART

General remarks, see ref. 21

Bis(3,5-dimethyl-2-furyl)ketone (**10**). 2,4-Dimethylfuran (9.4 g, 0.098 mol)[10] in anhydrous ether (10 ml) was added dropwise to a stirred solution of BuLi (1.4 M in hexane, 70 ml, 0.098 mol) cooled to -20°C under Ar atmosphere. The mixture was allowed to warm to 20°C and was then heated under reflux for 4 h, giving a dark red solution. After cooling to -20°C, methyl *N,N*-dimethylcarbamate (5.73 g, 0.049 mol) was added dropwise. Under stirring at -10°C for 45 min, the mixture was allowed to warm up to 5°C and a saturated aqueous solution of NH_4Cl (100 ml) was added. The organic layer was collected and the aqueous phase was extracted with CH_2Cl_2 (30 ml, twice). The combined organic extracts were dried ($MgSO_4$) and the solvent was evaporated in vacuo. The dark orange residue was purified by flash chromatography on silica gel (100 g, AcOEt/light petroleum 1:24), yielding 6.54 g (61%), yellowish crystals, mp 54-56°C (light petroleum/EtOAc). Uv (MeCN) λ_{max}: 294 (ε = 5700), 328 (11000); uv (isooctane) λ_{max}: 290 (4400), 300 (4900), 312 (8700), 326 (9500). Ir (KBr) ν: 2960, 2920, 1600, 1530, 1400, 1370, 1305, 1270, 1230, 990, 960, 890, 830, 810, 760, 740 cm^{-1}. ^{1}H-Nmr (250 MHz, $CDCl_3$) δ_H: 6.06 (*q*, ^4J = 0.5, 2 H); 2.37 (*d*, ^4J = 0.5, 2 Me-C(5)); 2.36 (*s*, 2 Me-C(3)). ^{13}C-Nmr (62.9 MHz, $CDCl_3$) δ_C: 171.8 (*s*, CO); 155.2 (*s*, C(2)); 146.8 (*s*, C(5)); 133.5 (*s*, C(4)); 112.5 (*d*, C(3)); 13.9, 12.2 (2*q*, 4 Me). Ms (70 eV) m/z: 218 (0.8, $M^{+\cdot}$), 203 (0.8), 191 (0.8), 167 (1.6), 149 (11), 119 (2), 97 (4), 83 (5), 71 (10), 69 (10), 58 (100), 55 (16). Anal. Calcd for $C_{13}H_{14}O_3$: C 71.54, H 6.47. Found: C 71.50, H 6.49.

1,1-Bis(3,5-dimethyl-2-furyl)ethene (**11**). A 1.4 M solution of BuLi in hexane cooled to -30°C (0.4 ml) was added dropwise to a stirred suspension of methyltriphenylphosphonium bromide (0.245 g, 0.75 mmol) in anhydrous THF (5 ml) cooled to -30°C under Ar atmosphere. After stirring the yellow mixture at -30°C for 90 min, a solution of **10** (0.106 g, 0.48 mmol) in anhydrous THF (5 ml) was added dropwise under stirring, maintaining the reaction mixture between -30 and -20°C (*ca.* 1 h). After stirring the orange solution at -25°C for 2 h, the mixture was allowed to warm up slowly to 20°C and it was filtered through a short column of silica gel (4 g, rinsing with AcOEt/light petroleum 1:6, R_f 0.65). After solvent evaporation, 94 mg (90%) of a yellow oil was obtained. This compound could be kept under Ar at -20°C for several weeks without decomposition. Uv (MeCN) λ_{max}: 257 (ε = 3500), 281 (6100); uv (isooctane): 258 (3300); 282 (5600). Ir (CH_2Cl_2) ν: 3100, 2950, 2920, 2870, 1630, 1590, 1570, 1540, 1450, 1405, 1380, 1310, 1180, 1150, 1130, 1100, 1070, 1000, 980, 950, 880, 810 cm^{-1}. ^{1}H-Nmr (250 MHz, $CDCl_3$) δ_H: 5.88 (*q*, ^4J = 0.8, 2 H-C(4')); 5.36 (*s*, $H_2C(2)$); 2.28 (*d*, ^4J = 0.8, 2 Me-C(5')); 1.83 (*s*, 2 Me-C(3')). ^{13}C-Nmr (62.9 MHz, $CDCl_3$) δ_C: 150.6 (*s*, C(5')); 146.1 (*s*, C(2')); 128.8 (*s*, C(3')); 119.3 (*s*, C(1)); 112.2 (*t*, C(2)); 110.5 (*d*, C(4')); 13.6, 10.5 (2*q*, Me-C(3'), Me-C(5')). Ms (70 eV) m/z: 216 (53.5, $M^{+\cdot}$), 203 (64), 201 (51), 173 (33), 153 (5), 149 (12), 123 (100), 121 (59), 115 (11), 111 (20), 109 (17), 107 (10), 96 (12), 95 (5), 85 (63), 83 (50), 77 (33), 57 (33), 55 (19).

*(1*RS,2SR,3RS*)-5-(3',5'-Dimethylfur-2'-yl)-1,8-dimethyl-7-oxabicyclo[4.3.0]nona-5,8-diene-2,3-dicarboxylic Anhydride* (**12**). A mixture of maleic anhydride (45 mg, 0.46 mmol), ether (0.3 ml) and **11** (102 mg, 0.47 mmol) was stirred at 20°C for 3 days. After the slow addition of light petroleum, 100 mg (80%) of yellow crystals were obtained. An analytical sample was recrystallized from ether/light petroleum, light yellow crystals, mp 143-145°C. Uv (MeCN) λ_{max}: 280 nm (ε = 13200). Ir (CH_2Cl_2) ν: 3050, 3020, 2970, 2920, 2860, 1850, 1780, 1700, 1660, 1640, 1610, 1560, 1440, 1380, 1140, 1090, 1060, 960, 905 cm^{-1}. ^{1}H-Nmr (250 MHz, $CDCl_3$) δ_H: 5.83 (*s*, H-C(9)); 5.20 (*q*, ^4J = 1.2, H-C(4')); 3.50 (*m*, H-C(3)); 3.37 (*dd*, ^2J = 16, ^3J = 5.5, H-C(4) *anti* with respect to H-C(3)); 2.79 (*dd*, ^2J = 16, ^3J = 5.5, H-C(4) *syn* with respect to H-C(3)); 2.25 (*ds*, Me-C(5')); 1.94 (*s*, Me-C(3')); 1.92 (*d*, ^4J = 1.2, Me-C(8)); 1.36 (*s*, Me-C(1)).[‡] ^{13}C-Nmr (62.9 MHz, $CDCl_3$) δ_C: 173.2, 170.3 (2*s*, 2 CO); 154.3, 153.2 (2*s*, C(2'), C(5')); 151.0 (*s*, C(6)); 143.1 (*s*, C(8)); 118.8 (*s*, C(3')); 110.3 (*d*, C(4')); 105.3 (*d*, C(9)); 98.4 (*s*, C(5)); 50.4, 39.7 (2*d*, C(2), C(3)); 48.1 (*s*, C(1)); 25.7 (*q*, *Me*-C(1)); 25.2 (*t*, C(4)); 13.6, 13.4, 11.2 (3*q*, *Me*-C(8), *Me*-C(3'), *Me*-C(5')). Ms (70 eV) m/z: 314 (53, $M^{+\cdot}$), 299 (39), 272 (10), 227 (14), 216 (22), 201 (100), 186 (11), 183 (12), 173 (31), 169 (11), 157 (11), 145 (15), 128 (20),

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[‡] Attributions confirmed by NOE measurements

115 (22), 104 (11), 99 (11), 91 (22), 89 (16), 77 (32), 65 (24), 55 (16). Anal. Calcd for $C_{18}H_{18}O_5$: C 68.78, H 5.77. Found: C 68.84, H 5.74.

*(1*RS,2SR,9SR*)-7-(3',5'-Dimethylfur-2'-yl)-2,4-dimethyl-5-oxatricyclo[7.4.0.0^{2,6}]trideca-3,6,11-triene-10,13-dione* (**13**). A mixture of **11** (59 mg, 0.27 mmol) and 1,4-benzoquinone (19 mg, 0.17 mmol) was stirred in the dark at 20°C for 3 days. The ^{1}H-nmr spectrum of the crude mixture showed 80% of conversion of **11**. Column chromatography on silica gel (4 g, AcOEt/light petroleum 1:24, then pure AcOEt) failed to give pure adduct, thus **13** could be characterized only by its ^{1}H-nmr spectrum taken on the crude reaction mixture. ^{1}H-Nmr (250 MHz, $CDCl_3$) δ_H: 6.64, 6.60 (*2d*, ^3J = 10, H-C(11), H-C(12)); 5.83 (*q*, ^4J = 0.8, H-C(4')); 4.90 (*q*, ^4J = 1.3, H-C(3)); 3.42-3.10 (*m*, H-C(1), H-C(8), H-C(9)); 2.57 (*dd*, ^2J = 17.0, ^3J = 5.5, H-C(8)); 2.24 (*d*, ^4J = 0.8, Me-C(5')); 1.93 (*s*, Me-C(3')); 1.90 (*d*, ^4J = 1.3, Me-C(4)); 1.85 (*s*, Me-C(2)).

*(1*RS,2RS*)-2-Cyano-5-(3',5'-dimethylfur-2'-yl)-1,8-dimethyl-7-oxabicyclo[4.3.0]nona-5,8-dien-2-yl Acetate* (**14**) and *(1*SR,2RS*)-2-cyano-5-(3',5'-dimethylfur-2'-yl)-1,8-dimethyl-7-oxabicyclo[4.3.0]nona-5,8-dien-2-yl Acetate* (**15**). A mixture of 1-cyanovinyl acetate (*Fluka*, 52 mg, 0.46 mmol) and **11** (101 mg, 0.47 mmol) was stirred at 20°C for 10 days. Column chromatography on silica gel (8 g, AcOEt/light petroleum 1:6) gave a first fraction (R_f = 0.41) yielding 8 mg (5%) of (**15**) and a second fraction (R_f = 0.29) that furnished 41 mg (27%) of **14**.

Characteristics of **14**: colorless, unstable crystals, mp 181-182°C (Et_2O/light petroleum). Uv (MeCN) λ_{max}: 273 nm (ε = 11800). Ir (CH_2Cl_2) ν: 3050, 2990, 2920, 2860, 2240, 1750, 1700, 1665, 1610, 1515, 1470, 1440, 1380, 1370, 1250, 1130, 1105, 1030, 990, 955, 910 cm^{-1}. ^{1}H-Nmr (250 MHz, $CDCl_3$) δ_H: 5.84 (*q*, ^4J = 0.5, H-C(4')); 5.13 (*q*, ^4J = 1.2, H-C(9)); 3.03-2.88 (*m*, H-C(3)); 2.64-2.55 (*m*, H-C(2)); 2.24 (*d*, ^4J = 0.5, *Me*-C(5')); 2.16 (*s*, Me-CO), 2.12-1.99 (*m*, H-C(2)); 1.97 (*s*, Me-C(3')); 1.94 (*d*, ^4J = 1.2, Me-C(8)); 1.35 (*s*, Me-C(1));‡ (attributions confirmed by a 360 MHz NOESY spectrum). ^{13}C-Nmr (62.9 MHz, $CDCl_3$) δ_C: 168.6 (*s*, CO); 155.3, 150.9, 150.7, 143.8 (4*s*, C(6), C(8), C(2'), C(5')); 118.8 (*s*, CN); 116.2 (*s*, C(3')); 110.0 (*d*, C(4')); 103.3 (*d*, C(9)); 100.0 (*s*, C(5)); 76.2 (*s*, C(2)); 52.7 (*s*, C(1)); 26.6, 22.0 (2*t*, C(3), C(4)); 22.5 (*q*, *Me*-CO); 21.0 (*q*, *Me*-C(1)); 11.3 (*q*, *Me*-C(3')); 13.6 (br. *q*, *Me*-C(8), *Me*-C(5')). Anal. Calcd for $C_{19}H_{21}NO_4$: C 69.71, H 6.47. Found: C 69.09, H 6.52.

Characteristics of **15**: yellowish oil. Uv (MeCN) λ_{max}: 275 nm (ε = 15800). Ir (CH_2Cl_2) ν: 3050, 2960, 2920, 2860, 2220, 1750, 1670, 1630, 1620, 1560, 1460, 1440, 1370, 1130, 1090, 1040, 1010, 990, 915. ^{1}H-Nmr (250 MHz, $CDCl_3$) δ_H: 5.86 (*q*, ^4J = 0.8, H-C(4')); 5.00 (*q*, ^4J = 1.2, H-C(9)); 2.86 (*m*, H-C(3)), 2.68 (*m*, H-C(3)); 2.52-2.25 (*m*, H-C(4)); 2.24 (*d*, ^4J = 0.8, Me-C(5')); 2.05 (*s*, Me-CO); 1.96 (*s*, Me-C(3')); 1.93 (*d*, ^4J = 1.2, Me-C(8)); 1.49 (*s*, Me-C(1)). ^{13}C-Nmr (62.9 MHz, $CDCl_3$) δ_C: 169.0 (*s*, CO); 153.8, 150.5, 150.3, 144.1 (4*s*, C(6), C(8), C(2'), C(5')); 118.6 (*s*, CN); 117.3 (*s*, C(3')); 110.2 (*d*, C(4')), 102.2 (*d*, C(9)); 99.2 (*s*, C(5)), 73.7 (*s*, C(2)); 52.9 (*s*, C(1)); 26.3, 21.5 (2*t*, C(3), C(4)); 25.5 (*q*, *Me*-CO); 21.0 (*q*, *Me*-C(1)); 13.6 (br. *q*, *Me*-C(8), Me-C(5')); 11.4 (*q*, Me-C(3')). Ms (70 eV) m/z: 327 (22, $M^{+\cdot}$), 284 (12), 258 (3), 216 (33), 201 (100), 173 (17), 159 (2), 121 (10), 91 (13), 77 (17), 69 (12), 57 (12), 55 (10).

8-[1-(3',5'-dimethylfur-2'-yl)-1,9-dimethyl-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (**16**). A solution of anthranilic and (155 mg, 0.11 mmol) in dimethoxyethane (0.5 ml) was added under stirring to a solution of **11** (69 mg, 0.31 mmol) and isopentyl nitrite (93 mg, 0.80 mmol) in $CHCl_3$ (0.1 ml) cooled to 0°C. After stirring at 0°C for 20 min, the temperature was rised quickly to 50°C and the mixture was stirred at 70°C for 10 min. *After cooling to 20°C, ether (15 ml) was added and the precipitate was filtered off.* The solvent was evaporated and the residue was purified by column chromatography on silica gel (8 g, AcOEt/light petroleum 1:12), yielding 10 mg (10%), yellow oil, that decomposes on storing at -20°C in a few days. Uv (MeCN) λ_{max}: 204 (ε = 23000), 272 (6800). ^{1}H-Nmr (250 MHz, $CDCl_3$) δ_H: 7.17-6.90 (*m*, 4 H arom.); 6.37 (*q*, ^4J = 1.8, H-C(10)); 6.02 (*d*, ^4J = 0.8, H-C(3')); 5.78, 5.45 (2*d*, ^2J = 1.3, H_2C=C); 2.29 (*d*, ^4J = 0.8, Me-C(5')); 2.15 (*s*, Me-C(3')); 1.92 (*s*, Me-C(1)); 1.75 (*d*, ^4J = 1.8, Me-C(9)). Ms (70 eV) m/z: 292 (26, $M^{+\cdot}$), 277 (12), 252 (92), 237 (16), 209 (21), 189 (10), 149 (15), 121 (100), 91 (40), 71 (62), 57 (85), 55 (56).

2-[2,2-Bis(3,5-dimethylfur-2-yl)ethenyl]benzoic Acid (**17**). Same procedure as for **16**, chromatography on silica gel (EtOAc/light petroleum 1:6), yielded one fraction; crystallization from ether/light petroleum gave yellow needles, mp 115-120°C (decomp.), that decompose into an oily product on storing at -20°C. Yield: 2-7%. Uv (MeCN) λ_{max}: 206 nm (ε = 24000), 228 (14000), 305 (8900), 344 (9500). Ir (CH_2Cl_2) ν: 3500, 3350-3000, 2960, 2920, 2650 (b), 2550 (b), 1770, 1730, 1690, 1610, 1590, 1560, 1475, 1450, 1410, 1110, 1060, 990, 960, 920, 805 cm^{-1}. ^{1}H-Nmr (250 MHz, $CDCl_3$) δ_H: 8.05 (*dd*, ^3J = 8.0, ^4J = 1.5, H-C(6)); 7.37 (*s*, H-C(1')); 7.29 (*m*, H-C(4), H-C(5)); 7.06 (*dd*, ^3J = 8.0, ^4J = 1.5, H-C(3)); 5.94, 5.78 (2 br *s*, H-C(4'''), H-C(4''), C(4'')); 2.32, 2.26 (2 br *s*, H-C(6'''), H-C(6'')); 1.64, 1.41 (2*s*, H-C(7'''), H-C(7'')). ^{13}C-Nmr (62.9

MHz, $CDCl_3$) δ_C: 172.6 (*s*, CO); 151.4, 151.2, 146.9, 144.4 (4*s*, quat. C of the furyl rings); 140.7 (*s*, C(2')); 132.0, 131.1, 126.6, 126.3 (4*dd*, C(3), C(4), C(5), C(6)); 130.5 (*d*, C(1')); 127.57 (*s*, C(1)); 122.0 (*s*, C(2)); 120.8, 120.6 (2*s*; 111.5, 109.8 (2*d*); 13.7, 13.3, 10.3, 9.9 (4*q*, methyl groups of the furyl rings). Ms (70 eV) m/z: 336 (100), 303 (26), 233 (26), 201 (45), 165 (17), 123 (7), 118 (16), 77 (20).

Dimethyl 4-[1-(3',5'-dimethylfur-2'-yl)ethenyl]-1,5-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**18**) and *Dimethyl 5-[1-(3',5'-dimethylfur-2'-yl)-1,8-dimethyl-7-oxabicyclo[4.3.0]nona-2,5,8-triene-2,3-dicaboxylate* (**19**). A mixture of **11** (142 mg, 0.65 mmol) and dimethyl acetylenedicarboxylate (93 mg, 0.65 mmol) was stirred at 20°C for 3 days. Column chromatography on silica gel (12 g, AcOEt/light petroleum 1:6) gave a first fraction ($R_f = 0.33$, AcOEt/light petroleum 1:6) containing 120 mg (48%) of **19**, and a second fraction ($R_f = 0.23$) affording 30 mg (12%) of **18**.

Characteristics of **18**: yellow oil, decomposes on storing at room temperature. Uv (MeCN) λ_{max}: 240 nm (ε = 10700), 343 (12150). Ir (CH_2Cl_2) ν: 3040, 2980, 2950, 2920, 2880, 1720, 1610, 1550, 1470, 1400, 1370, 1240, 1210, 1160, 1060, 990, 900, 810 cm^{-1}. ^{1}H-Nmr (250 MHz, $CDCl_3$) δ_H: 6.26, 5.27 (2*d*, ^2J = 1.0, H_2C=C); 5.91 (*d*, ^4J = 0.7, H-C(4')); 5.85 (*q*, ^4J = 0.7, H-C(6)); 3.69, 3.62 (2*s*, 2 MeO); 2.26 (*d*, ^4J = 0.7, Me-C(5')); 2.22 (*d*, ^4J = 0.7, Me-C(5)); 1.72, 1.61 (2*s*, Me-C(1), Me-C(3')). ^{13}C-Nmr (62.9 MHz, $CDCl_3$) δ_C: 169.3, 167.0 (2*s*, 2 CO); 153.3, 152.9 (2*s*, C(2'), C(5')); 144.8, 144.4 (2*s*, C(5), C(3')); 138.7 (*s*, CH_2=*C*); 128.5 (*t*, *C*H_2=C); 127.3 (*s*, C(4)); 77.3 (*s*, C(1)); 124.7, 124.5 (2*s*, C(2), C(3)); 111.6 (*d*, C(4')); 110.8 (*d*, C(1), C(6)); 52.0, 51.9 (2*q*, 2 MeO); 13.7, 13.6, 10.8, 10.3 (4*q*, *Me*-C(1), Me-C(5), Me-C(3'), Me-C(5')). Ms (70 eV) m/z: 358 (21, $M^{+\cdot}$), 327 (11), 326 (47), 311 (7), 284 (92), 267 (33), 266 (12), 253 (12), 252 (100), 242 (41), 241 (13), 223 (12), 210 (37), 165 (10).

Characteristics of **19**: slightly yellow oil, decomposes on storing at room temperature. Uv (MeCN) λ_{max}: 276 nm (ε = 13700). Ir (CH_2Cl_2) ν: 3040, 2960, 2920, 2880, 1720, 1670, 1630, 1560, 1430, 1380, 1350, 1300, 1200, 1150, 1130, 1100, 1080, 1040, 910, 810 cm^{-1}. ^{1}H-Nmr (250 MHz, $CDCl_3$) δ_H: 5.86 (*d*, ^4J = 0.7, H-C(4')); 5.03 (*q*, ^4J = 1.3, H-C(9)); 3.82, 3.14 (2*d*, ^2J = 21, H-C(4)); 3.83, 3.79 (2*s*, 2 MeO); 2.25 (*d*, ^4J = 0.7, Me-C(5')); 1.99 (*s*, Me-C(3')); 1.90 (*d*, ^4J = 1.3, *Me*-C(8)); 1.39 (*s*, *Me*-C(1)). ^{13}C-Nmr (62.9 MHz, $CDCl_3$) δ_C: 167.6, 166.8 (2*s*, 2 CO); 154.4, 154.3, 150.5 (3*s*, C(6), C(8), C(2'), C(5')); 143.6, 143.4 (2*s*, C(2), C(3)); 131.0 (*s*, C(3')); 110.2 (*d*, C(4')); 103.8 (*d*, C(9)); 98.5 (*s*, C(5)); 52.3, 52.2 (2*q*, 2 MeO); 50.3 (*s*, C(1));

28.7 (*t*, C(4)); 27.0, 13.6, 13.5, 11.3 (4*q*, *Me*-C(1), *Me*-C(8), *Me*-C(3'), *Me*-C(5')).

2-[3,3-Bis(3,5-dimethylfur-2-yl)cyclobutylidene]acetic Acid (**20**). A mixture of **11** (79 mg, 0.36 mmol), buta-2,3-dienoic acid (29 mg, 0.34 mmol) and ether (0.1 ml) was stirred at 20°C for 3 days. Column chromatography on silica gel (AcOEt/light petroleum 1:4, then pure AcOEt) afforded 33 mg (32%), honey-like, yellowish product. Uv (MeCN) λ_{max}: 220 nm (ε = 16500), 286 (2020). Ir (CH_2Cl_2) ν: 3050, 3000, 2960, 2920, 2880, 2650, 2550, 1770, 1700, 1660, 1610, 1570, 1430, 1400, 1240, 1160, 1110, 1040, 1000, 950, 880, 810 cm^{-1}. ^1H-Nmr (250 MHz, $CDCl_3$) δ_H: 5.73 (*m*, H-C(2), 2 H-C(4')); 3.86, 3.58 (2 br *d*, ^4J = 2.0, 2 H_2C of cyclobutylidene); 2.23 (br *s*, 2 Me-C(5')); 1.64 (*s*, 2 Me-C(3')). ^{13}C-Nmr (62.9 MHz, $CDCl_3$) δ_C: 171.9 (*s*, CO); 165.7 (*s*, C(sp^2) of cyclobutylidene); 149.0, 148.8 (2*s*, C(2'), C(5') of furyl groups); 115.9 (*s*, C(3')); 113.3 (*d*, C(2)); 110.2 (*d*, C(4') of furyl groups); 45.3, 43.5 (2*t*, 2 H_2C of cyclobutylidene); 38.6 (*s*, C quat. of cyclobutylidene); 13.5, 9.8 (2*q*, 4 Me). Ms (70 eV) m/z: 300 (18, $M^{+\cdot}$), 286 (16), 285 (22), 267 (3), 257 (9), 243 (11), 240 (13), 205 (61), 204 (11), 201 (15), 197 (15), 159 (14), 145 (10), 133 (7), 128 (13), 125 (12), 115 (30), 109 (24), 105 (19), 99 (25), 97 (23), 91 (47), 85 (69), 77 (50), 57 (100). Anal. Calcd for $C_{18}H_{20}O_4$: *C 71.98, H 6.71. Found: C 71.85, H 6.75.*

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Received, 24th August, 1992