HETEROCYCLES, Vol. 57, No. 8, 2002, pp. 1513 - 1524, Received, 13th June, 2002

SYNTHESIS OF 2,2',2'',2'''-(1,2-ETHANEDIYLIDENE)TETRAFURAN AND DIELS-ALDER REACTION WITH DIMETHYL ACETYLENE-DICARBOXYLATE

Marc-Etienne Schwenter,[a] Kurt Schenk,[b] Rosario Scopelliti,[a] and Pierre Vogel[a,]*

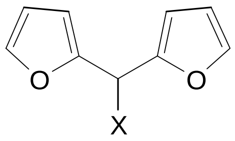
[a] Institute of Molecular and Biological Chemistry, Swiss Federal Institute of Technology, EPFL-BCH, CH-1015 Lausanne-Dorigny, Switzerland, Fax +41 21 693 93 75; e-mail: pierre.vogel@epfl.ch

[b] Institute of Crystallography, University of Lausanne, BSP, CH-1015 Lausanne-Dorigny, Switzerland

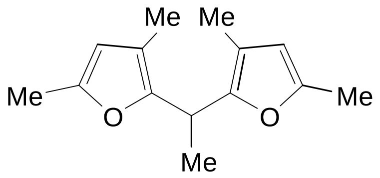
Abstract - A one step procedure has been found that converts 2,2'-methylenedifuran (**1**) into 2,2,',2'',2'''-(1,2-ethanediylidene)tetrafuran (**4**: 1,1,2,2-tetrakis(furan-2-yl)ethane). This compound adopts two similar C_{2V}-symmetrical conformations (**4A** and **4A'**) in the crystalline state in which the C-H bond of the 1,2-ethanediylidene moieties is *anti*-periplanar with the C(2)-O bond of the vicinal furan-2-yl groups. Tetrafuran (**4**) is little reactive toward dienophiles with normal electronic demand. With dimethyl acetylenedicarboxylate a single 1:1 adduct (**8**) (dimethyl (1*RS*,2*RS*,2a*RS*,5*SR*,5a*RS*,6*RS*,8a*RS*,8b*SR*)-1,2-di(furan-2-yl)-1,2-dihydro-5*H*,6*H*-2a,5:6,8a-diepoxyacenaphthylene-5a,8b-dicarboxylate) was isolated. Its structure was established by single crystal X-Ray radiocrystallography.

INTRODUCTION

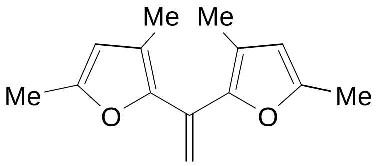
We have shown that long-chain 1,3-polyols (polyketides) can be obtained *via* the double [4+3]-cycloaddition of 1,1,3-trichloro-2-oxyallyl cation to 2,2'-methylenedifuran (**1**).[1,2] Our group has reported also that long-chain polypropionates can be prepared through Diels-Alder additions of 2,2'-ethylidenebis[3,5-dimethylfuran] (**2**).[3,4] Earlier we had shown that the cycloadditions of 1,1-bis(3,5-dimethylfur-2-yl)ethene (**3**) have chemoselectivities depending strongly on the nature of the dienophiles.[5] During our exploration of the reactivity of the bisfuryl derivative (**1**) we discovered a possibility to convert it into the yet unknown 2,2',2",2'"-(1,2-ethanediylidene)tetrafuran (**4**). To our knowledge only derivative (**5**) had been reported as the first member of this tetrafuryl family. It was obtained by one-electron oxidation of 1,1-bis[(5-trifluoroacetyl)fur-2-yl]ethane by cupric salts.[6] We report the synthesis of **4** and on its Diels-Alder reactivity toward dimethyl acetylenedicarboxylate. X-Ray diffraction studies on **4** demonstrate that this compound adopts a C_{2V}-symmetrical conformation in the crystalline state with the C_2-axis cutting the middle of the σ(C-C) bond of the ethanediylidene moiety and with the furyl groups eclipsing the C-H bond of the ethanediylidene moiety.



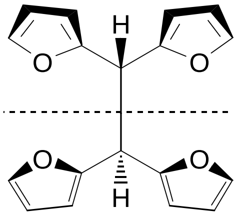
1 X = H
6 X = Cl
7 X = Me_3Si



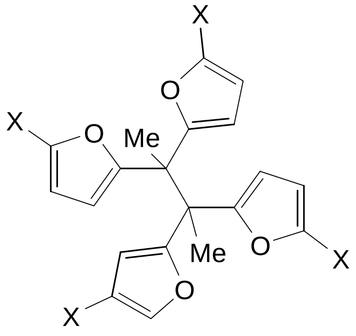
2



3



4A (CH/CO*anti*)
C_{2V}



5 X = CF_3CO

RESULTS AND DISCUSSION

Treatment of **1** with 1.1 equivalent of butyllithium in anhydrous THF at –78°C gave the corresponding product of hydrogen/metal exchange. Attempts to quench it with electrophilic chlorinating agents (NCS, Cl_2) all failed to give the expected chloro derivative (**6**), but generated intractable tars. Quenching with hexachloroethane led to the exclusive formation of **4** and polymeric material. Compound (**4**) was isolated in 51% yield. Its structure was given by its spectral data, elemental analysis and by X-Ray diffraction studies (see below). Quenching the lithiated **1** with trimethylsilyl chloride gave silane (**7**) in 74% yield. The molecular structure of **4** in the crystalline state is represented in Figure 1 (see Table 1). It shows two similar C_{2V}-symmetrical conformers (**4A**) and (**4A'**). As expected for steric reasons (Pitzer strain), the 1,1,2,2-tetrasubstituted ethane system adopts staggered *anti*-conformations that minimize repulsions between the four furyl moieties. This was also reported for 1,1,2,2-tetraphenylethane.[8] The orientation adopted by the furan rings makes them to eclipse the C-H bonds of the ethanediylidene moiety, as expected for isopropyl and other alkyl substituents of alkenes and arenes.[9] It is interesting to note that the C_{2V}-conformer (**4B**), the C_2-conformer (**4C**), and the centro-symmetric conformer (**4D**) are not present in the crystalline state. The selection of conformers (**4A** and **4A'**) in the crystalline state might also be the result of lattice effect. Conformational analysis of **4** in the gas phase will have to be carried out before concluding on the origin of the preference for conformations (**4A**, **4A'**) in the crystalline state.

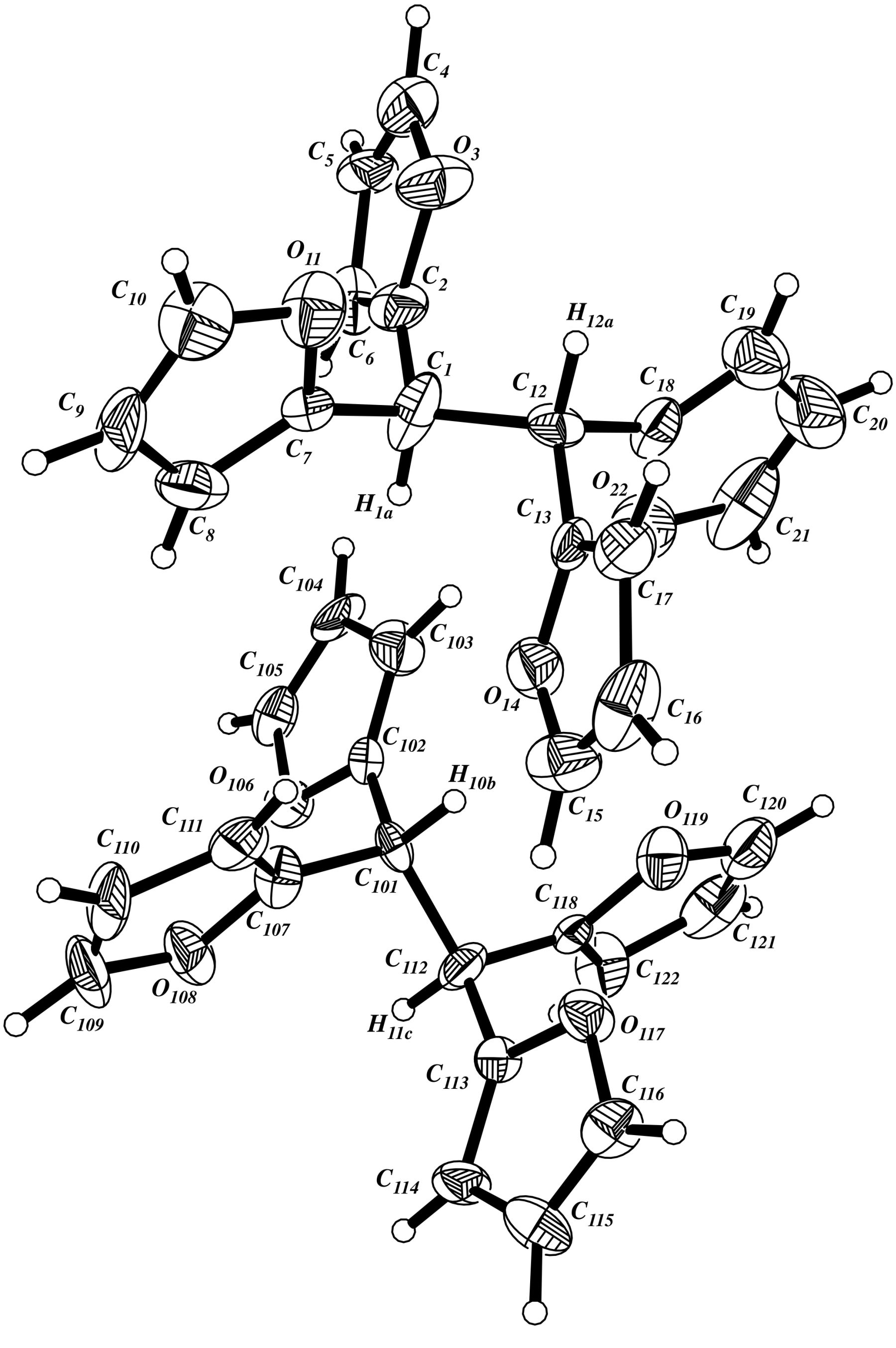
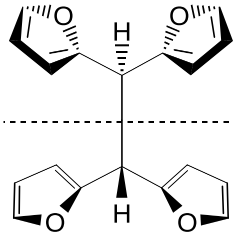
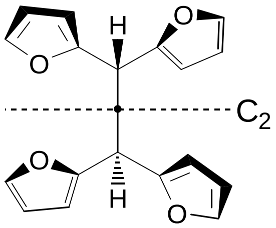


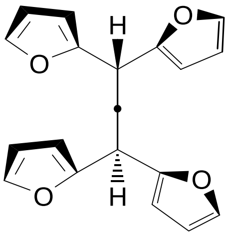
Figure 1. ORTEP representation[7] of the two C_{2V}-conformers (**4A** and **4A'**) found in the crystalline state. For reasons of commodity, the atom numbering does not follow the IUPAC rules.



4B (CH/CO*syn*)
C_{2V}



4C (C_2-axis)



4D (centrosymmetric)

Table 1. Selected bond lengths, interactomic separations and torsion angles for **4A** and **4A'**.

Bond distances (Å)					
C1-C2	1.499(12)	C1-C12	1.5118(6)	C1-C7	1.446(10)
C7-C8	1.775(12)	C8-C9	1.456(14)	C9-C10	1.32(2)
C10-O11	1.410(13)	C7-O11	1.327(10)	C1-C12	1.518(6)
C101-C112	1.547(6)	C110-C111	1.432(13)	C103-C104	1.435(11)
C114-C115	1.463(11)				
Interatomic distances (Å)					
O3-O11	3.108(0.011)	O3-O22	4.260(0.012)	O3-O14	5.214(0.006)
O11-O14	4.176(0.011)	O11-O22	5.300(0.007	O14-O22	3.170(0.013)
O106-O108	2.978(0.010)	O106-O119	4.322(0.008)	O106-O117	5.298(0.004)
O108-O117	4.319(0.008)	O108-O119	5.221(0.005)	O117-O119	3.019(0.011)

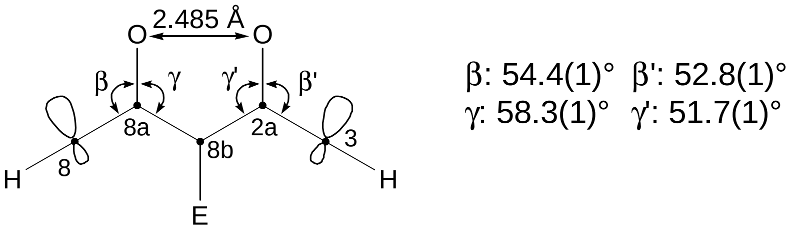
Selected torsion angles in degrees					
C2-C1-C12-C18	45.04	(0.98)	C102-C101-C112-C118	-50.22	(0.68)
C2-C1-C12-C13	175.21	(0.98)	C102-C101-C112-C113	-179.69	(0.99)
C2-C1-C12-H12A	-69.65	(0.73)	C102-C101-C112-H11C	64.71	(0.54)
H1A-C1-C12-C18	-66.01	(0.64)	C107-C101-C112-C118	-178.27	(0.85)
H1A-C1-C12-C13	64.16	(0.57)	C107-C101-C112-C113	52.26	(0.66)
H1A-C1-C12-H12A	179.30	(0.01)	C107-C101-C112-H11C	-63.35	(0.47)
C7-C1-C12-C18	-177.36	(1.09)	H10B-C101-C112-C118	65.44	(0.55)
C7-C1-C12-C13	-47.20	(0.99)	H10B-C101-C112-C113	-64.03	(0.60)
C7-C1-C12-H12A	67.94	(0.78)	H10B-C101-C112-H11C	-179.63	(0.00)

The tetrafuryl derivative (**4**) is much less reactive than simpler furan derivatives[10] in Diels-Alder reactions. With maleic anhydride,[11] **4** refused to equilibrate with any adduct, even after 5 days at 50°C. In 5 molar $LiClO_4$ ether, **4** reacted with maleic anhydride at 25°C giving intractable tars. With dimethyl acetylenedicarboxylate and without Lewis acid promoter, a complex mixture of product was formed slowly at 20-40°C. As no major product could be formed selectively under these conditions, we treated **4** with dimethyl acetylenedicarboxylate in the presence of $LiClO_4$ in ether[12] at 20°C. After 20 h and *ca.* 40% conversion of **4**, a major product (**8**) was formed and could be purified by flash chromatography on silica gel and isolated in 34% yield.[13] It consisted of a 1:1 adduct of **4** and dimethyl acetylenedicarboxylate, the structure of which was deduced from its spectral data and by single crystal X-Ray radiocrystallography (Figure 2, Table 2). Attempts to generate a 1:2 adduct of **4** and dimethyl acetylenedicarboxylate applying high pressure (1200 and 1950 MPa, $LiClO_4/Et_2O$) led to complex mixtures of products of high molecular mass from which no single compound could be isolated.

Table 2 Selected bond lengths, torsion angles and angles between averaged planes of **8**

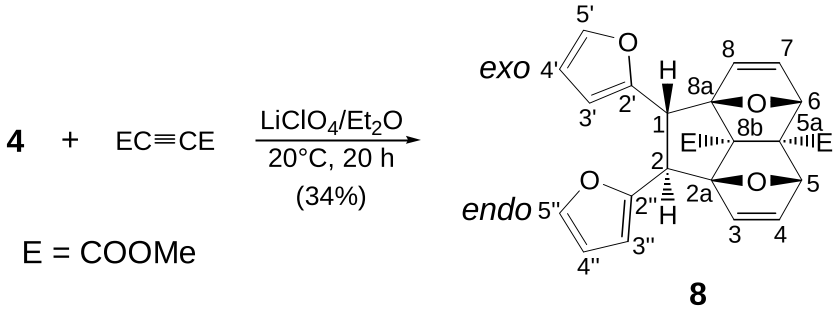
bond lengths in Å					
C(1)-C(2)[a)]	C11-C12[b)]	1.594(2)	C(5a)-C(8a)[a)]	C1-C6[b)]	1.548(2)
C(1)-C(8a)	C10-C12	1.539(2)	C(8a)-C(8b)	C6-C10	1.577(2)
C(2)-C(2a)	C5-C11	1.529(2)	C(2a)-C(8b)	C5-C6	1.571(2)
C(1)-C(2’)	C12-C21	1.483(2)	C(5a)-C(6)	C1-C7	1.575(2)
C(2)-C(2’’)	C11-C17	1.490(2)	C(5)-C(5a)	C1-C2	1.600(2)
C(8a)-C(8)	C9-C10	1.520(2)	C(6)-C(7)	C7-C8	1.528(3)
C(2a)-C(3)	C4-C5	1.514(2)	C(4)-C(5)	C2-C3	1.529(2)
C(3)-C(4)	C3-C4	1.327(3)	C(7)-C(8)	C8-C9	1.330(3)

Torsion angles in degrees			
C(8a)-C(1)-C(2’)-O(1’)[a)]	C10,C12,C21,O8[b)]	-121.25(17)	C(1)-H/furanyl eclipsed
C(2)-C(1)-C(2’)-O(1’)	C11,C12,C21,O8	116.90(16)	
C(2a)-C(2)-C(2’’)-O(1’’)	C12,C11,C17,O7	177.26(15)	C(2)-H/furanyl bisecting
C(1)-C(2)-C(2’’)-O(1’’)	C5,C11,C17,O7	55.3(2)	
C(8a)-C(1)-C(2)-C(2a)	C10,C12,C11,C5	-8.38(17)	Twisted cyclopentane
C(2)-C(1)-C(8a)-C(8b)	C11,C12,C10,C6	-16.98(17)	



a) IUPAC atom numbering, see structure (**8**).

b) Atom numbering used in Figure 2



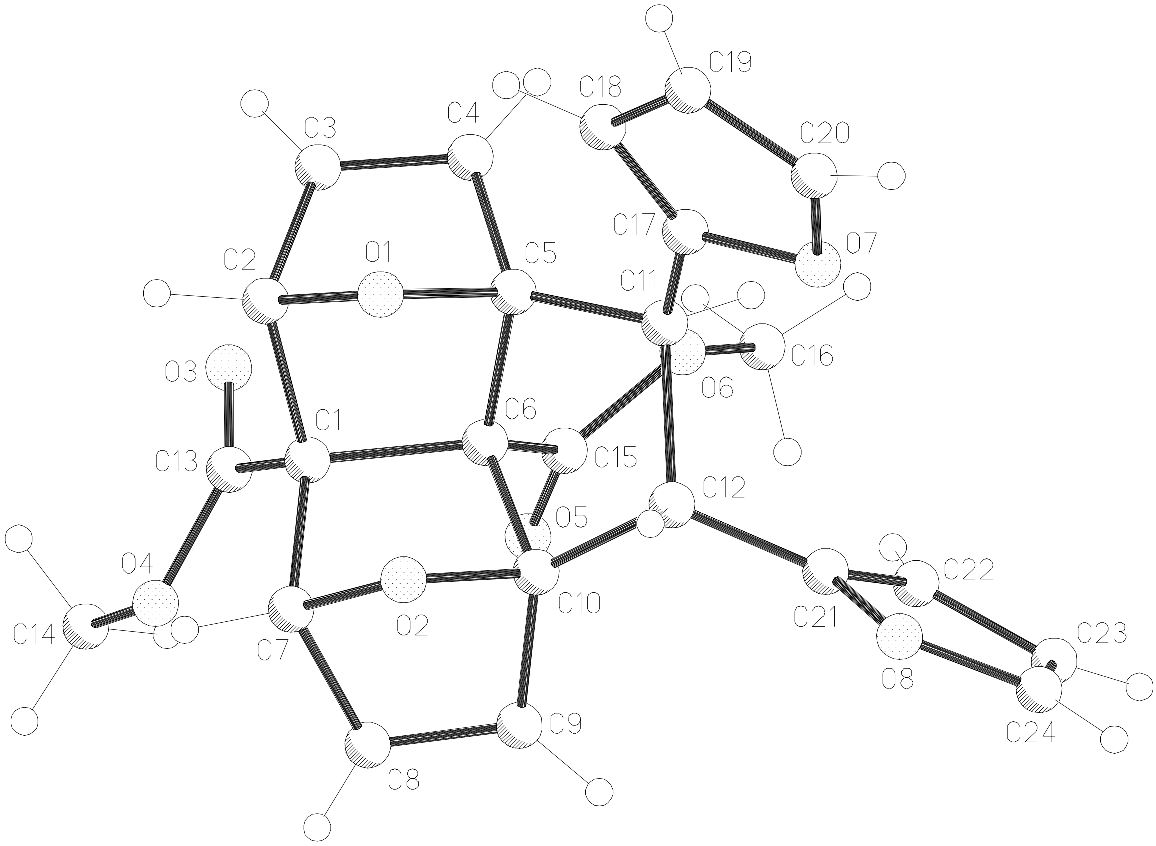
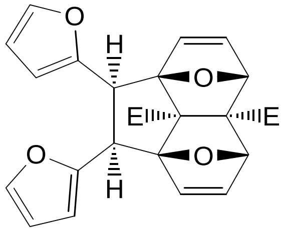


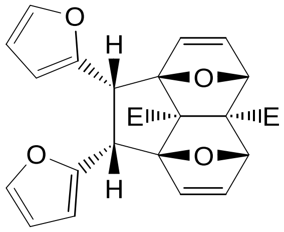
Figure 2. ORTEP representation[7] of adduct (**8**). For reasons of commodity the atom numbering does not follow the IUPAC rules.

No isomeric forms (**9**-**11**) of adduct (**8**) could be seen in the ^{1}H-NMR spectrum of the crude reaction mixture of **4** with dimethyl acetylenedicarboxylate (LiClO$_4$, 20°C). As for most furan derivatives, their Diels-Alder additions are reversible, thus **8** might correspond to the most stable Diels-Alder product between **4** and dimethyl acetylenedicarboxylate. The high-molecular weight material that forms under forcing conditions arises probably from Michael additions of the furan moieties of **4** and **8**.[10]

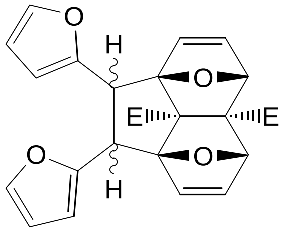
The X-Ray data for **8** shows that the "*endo*"-O(1''),C(2'',3'',4'',5'')-furan-2-yl adopts a staggered conformation with its ring *syn*-periplanar with the adjacent C(2)-H bond (C(12) in Figure 2) whereas the "*exo*"-O(1'),C(2',3',4',5')-furan-2-yl moiety (at C(11) in Figure 2) adopts a nearly bisected conformation with the adjacent C(1)-H bond. This is probably due to the fact that the oxygen atom or the C(5')-H bond of this furan-2-yl moiety would get too close to the adjacent 7-oxa ethereal bridge if a “normal” staggered conformation (as for **4** and the other furan-2-yl ring of **8**) should prevail. Distance between H-C(18) and O(1) (Figure 2) is evaluated to 2.655 Å, which is already relatively short. Most interesting is the observation of long allylic C-C bonds σ(C(2a),C(8b)), σ(C(8),C(8b)), σ(C(5),C(5a)) and σ(C(5a),C(6)) of 1.571(2), 1.577(2), 1.600(2) and 1.575(2) Å, respectively, to be compared with the “normal” σ(C(5a),C(8b)) bond of 1.548 Å. This phenomenon had been noticed by neutron diffraction measurements of *exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride[14] and that has been interpreted by us as the manifestation that bicyclo[2.2.1]hept-2-ene and 7-oxabicyclo[2.2.1]hept-2-ene systems admit in their ground state some properties of their products of retro-Diels-Alder cycloreversion (hyperconjugation model[15]). Interesting also is the C(1), C(2), C(2a), C(8b), C(8a) cyclopentane ring of **8** that adopts a twist conformation (Table 2) with carbon centres C(8b) and C(2a) lying above and below, respectively of the plane of C(8a),C(1),C(2). In 7-oxabicyclo[2.2.1]hept-2-ene systems angle β between average plane containing the bridgehead centre and the alkene moiety with the ethereal moiety (plane C(1)-O(7)-C(4)) is significantly larger than angle γ between the same ethereal moiety and average plane C(1)-C(6)-C(5)-C(4).[16] In the case of **8**, this is not the case as a result of the repulsion between the two *syn* 7-oxa bridges separated by short distance of 2.485 Å (Table 2).



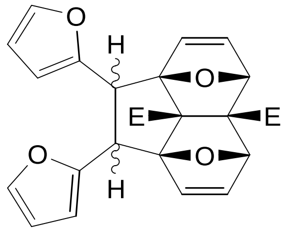
9a (*meso*)



9b (*meso*)



10



11

CONCLUSION

An efficient synthesis of 2,2’,2’’,2’’’-(1,2-ethanediylidene)tetrafuran (**4**) has been developed starting from furfuryl alcohol and furan[1] (2 steps). This new tetrafuran adopts a C_{2V}-symmetrical conformation in the crystalline state. It is not a reactive diene in Diels-Alder additions. Nevertheless a 1:1 adduct of **4** with dimethyl acetylenedicarboxylate has been isolated. It involves a “pincer” tandem Diels-Alder addition in which two vicinal furan rings add in a *syn* fashion of the acetylenic dienophile.

ACKNOWLEDGMENTS

This work was supported by the *Swiss National Science Foundation*, the *Fonds Herbette* (Lausanne), the *Office Fédéral de l'Education et de la Science* (European COST D13/010/01 project). We are grateful also to Mr. Martial Rey and Francisco Sepúlveda for their technical help.

EXPERIMENTAL

General, see ref. 17

2,2’,2’’,2’’’-(1,2-Ethanediylidene)tetrafuran (**4**). 2,2’-Methylenedifuran (**1**) (3 g, 20 mmol) was dissolved in anhydrous THF (100 mL). The mixture was cooled under N_2 to -78°C and BuLi (1.57 M in hexane, 14 mL, 22 mmol) was added dropwise. After 1 h the lithiated derivative was reacted with a solution of hexachloroethane (5.21 g, 22 mmol) in THF (10 mL). During the overnight reaction, the temperature was allowed to reach slowly 20°C. The solution was then treated with 5% aqueous $NaHSO_4$ (50 mL) and successively washed with H_2O (50 mL) and brine (50 mL). The aqueous phases were extracted with ether (10 mL, twice). The organic phases were collected and dried ($MgSO_4$). After solvent evaporation, the dark red residue was purified by flash chromatography on silica gel (light petroleum ether/Et_2O 9:1) to collect an orange oil which solidifies. The latter can be crystallised from heptane (50 mL) furnishing pure **4** (1.5 g, 51%), colorless crystals, mp 117-118°C (heptane). UV (MeCN): λ_{max} = 230 nm (ε = 8300 $M^{-1}cm^{-1}$). IR (KBr) ν: 3150, 3120, 1600, 1515, 1380, 1250, 1210, 1145, 1065, 1015, 955, 885, 770, 740, 720, 595, 540 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.29 (*d*, ^3J = 1.0, H-C(5,5’)), 6.22 (*dd*, ^3J = 3.2, ^3J = 1.8, H-C(4,4’)), 6.03 (*d*, ^3J = 3.1, H-C(3,3’)), 4.92 (*s*, H-C(6)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ_C 152.6 (*s*, C(2,2’)), 141.5 (*d*, ^1J(C,H) = 202, C(5,5’), 110.2 (*d*, ^1J(C,H) = 175, C(4,4’)), 107.0 (*d*, ^1J(C,H) = 175, C(3,3’)), 42.8 (*d*, ^1J(C,H) = 132, C(6)). MS-CI (NH_3): 148 (19, $[M\text{-}35]^+$), 147 (100, $[M/2]^+$), 118 (4), 91 (45), 89 (12). Anal. Calcd for $C_{18}H_{14}O_4$: C 73.46, H 4.79. Found: C 73.53, H 4.88. Crystal for X-Ray diffraction, see Table 3.

Table 3. Crystal data and structure refinement for **4A**, **4A’**

Empirical formula	$C_{18}H_{14}O_4$	
Formula weight	294.29	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.007(2) Å	α= 77.88(3)°
	b = 9.022(2) Å	β= 73.51(3)°
	c = 11.319(2) Å	γ = 78.48(3)°
Volume	758.0(3) $Å^3$	
Z	2	
Density (calculated)	1.289 Mg/m^3	

Table 3 (continued)

Absorption coefficient	0.091 mm^{-1}
F(000)	308
Crystal size	n/a
Theta range for data collection	3.66 to 24.99°
Index ranges	-10<=h<=11, -12<=k<=11, -14<=l<=76
Reflections collected	3632
Independent reflections	3106 [R(int) = 0.0269]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3103 / 30 / 397
Goodness-of-fit on F^2	1.661
Final R indices [I>2sigma(I)]	R1 = 0.0774, wR2 = 0.2082
R indices (all data)	R1 = 0.0956, wR2 = 0.2206
Weight	$[\ \sigma^2(F_o,^2\ ) + (0.1 * P)^2]^{-1}$
Absolute structure parameter	1(3) ∅ meaningless
Largest diff. peak and hole	0.314 and -02.32 e.Å^{-3}

2,2’-(Trimethylsilylmethylene)difuran (**7**). 2,2’-Methylenedifuran (**1**) (3 g, 20 mmol) was dissolved in anhydrous THF (100 mL). After cooling to -78°C, BuLi (1.57 M in hexanes, 14 mL, 22 mmol) was added dropwise. After stirring at -78°C for 1 h, Me$_3$SiCl (4.35 g, 40 mmol) was added and the mixture stirred at -78°C for 30 min. A saturated solution of NH$_4$Cl in MeOH (10 mL) was added and the cooling bath removed. The mixture was stirred and allowed to warm up to 20°C. The organic phase was dried (MgSO$_4$) and the solvent evaporated under vacuum. Bulb-to-bulb distillation of the residue gave **7** (3.75 g, 74%), yellowish oil, bp 63°C/4 mbar. In the condensed state, **7** was polymerized slowly already at -25°C. ^{1}H-NMR (400 MHz, CDCl$_3$): δ_H 7.32 (*dd*, ^3J = 1.9, ^4J = 0.8, H-C(5,5’)), 6.31 (*dd*, ^3J = 3.0, 1.9, H-C(4,4’)), 6.02 (br d, *J* = 3.0, H-C(3,3’)), 3.75 (*s*, HC(methylene)), 0.07 (*s*, Me$_3$Si). ^{13}C-NMR (100.6 MHz, CDCl$_3$): δ_C 140.5 (*d*, ^1J(C,H) = 192, C(5,5’)), 154.2 (*s*, C(2,2’)), 110.3 (*d*, ^1J(C,H) = 170, C(4,4’)), 104.8 (*d*, ^1J(C,H) = 173, C(3,3’)), 32.0 (*d*, ^1J(C,H) = 121, CH-Si), 2.3 (*q*, ^1J(C,H) = 119, Me$_3$Si).

Dimethyl (1*RS*,2*RS*,2a*SR*,5*SR*,5a*RS*,6*RS*,8a*RS*,8b*SR*)-1,2-di-2-(furan-2-yl)-1,2-dihydro-5*H*,6*H*-2a,5:6,8a-diepoxyacenaphthylene-5a,8b-dicarboxylate (**8**). A mixture of anhydrous LiClO$_4$ (535 mg, 5 mmol), ether (1 mL) and **4** (60 mg, 0.2 mmol) was stirred at 20°C until complete dissolution. Dimethyl acetylenedicarboxylate (104 mg, 0.7 mmol) was added and the mixture stirred at 20°C for 20 h. Water (1 mL) was added and the mixture extracted with EtOAc (2 mL, 3 times). After drying ($MgSO_4$) and solvent evaporation the residue was purified by flash chromatography on silica gel (light petroleum ether/Et_2O 3:7) giving pure **8** (30 mg, 34%), colorless crystals, mp 126-127°C (light petroleum ether/EtO_2). UV (MeCN): λ_{max} = 222 nm (ε = 2200 M^{-1}cm^{-1}). IR (KBr) ν: 3435, 3145, 3110, 1730, 1725, 1505, 1435, 1285, 1265, 1115, 1080, 1015, 980, 965, 910, 770, 745, 730, 715, 680, 600, 555 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.38 (*m*, 2H, H-C(5',5'')), 6.86 (*d*, ^{3}J = 5.5, H-C(8) or H-C(3)), 6.69 (*dd*, ^{3}J = 5.5, 1.6, H-C(7) or H-C(4)), 6.68 (dd, ^{3}J = 5.5, 1.7, H-C(4) or H-C(7)), 6.39-6.24 (*m*, 4H, H-C(3',3'',4',4'')), 5.28 (*d*, ^{3}J = 1.6, H-C(6) or H-C(5)), 5.21 (d, ^{3}J = 1.5, H-C(5) or H-C(6)), 4.75 (d, ^{3}J = 7.4, H-C(2) or H-C(1)), 4.20 (d, ^{3}J = 7.4, H-C(1) or H-C(2)), 3.63, 3.58 (2*s*, 6H, 2 MeO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ_C 170.3, 169.8 (2*s*, 2 COO), 152.6, 151.3 (2*s*, C(2',2'')), 142.2, 142.0 (2*d*, ^{1}J(C,H) = 203, C(5'5'')), 139.9, 139.7 (2*d*, ^{1}J(C,H) = 180, C(4), C(7)), 137.9, 137.7 (2*d*, ^{1}J(C,H) = 179, C(3), C(8)), 110.5, 110.2 (2*d*, ^{1}J(C,H) = 176, C(4',4'')), 107.4, 106.9 (2*d*, ^{1}J(C,H) = 172, C(3',3'')), 98.5, 96.3 (2s, C(2a), C(8a)), 84.7, 83.7 (2*d*, ^{1}J(C,H) = 167, C(5), C(6)), 81.8 (*s*, C(5a)), 70.3 (*s*, C(8b)), 52.2, 52.0 (2*q*, ^{1}J(C,H) = 147, 2 MeO), 47.9, 46.9 (2*d*, ^{1}J(C,H) = 132, C(1), C(2)). MS-EI (MeCN/H_2O/AcOH) m/z: 437 (75, $M^{\bullet+}$), 392 (30), 289 (100), 273 (60). Crystal for X-Ray diffraction, see Table 4.

Table 4. Crystal data and structure refinement for adduct (**8**)

Empirical formula	$C_{24}H_{20}O_8$	
Formula weight	436.40	
Temperature	143(2) K	
Wavelength	0.71070 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.362(2) Å	α= 90°
	b = 12.051(2) Å	β= 105.77(3)°
	c = 14.949(3) Å	γ = 90°
Volume	1969.9(7) Å^3	
Z	4	
Density (calculated)	1.471 Mg/m^3	
Absorption coefficient	0.111 mm^{-1}	
F(000)	912	
Crystal size	0.16 x 0.14 x 0.11 mm^3	
Theta range for data collection	1.86 to 24.41°.	

Table 4 (continued)

Index ranges	-12<=h<=13, -13<=k<=14, -15<=l<=16
Reflections collected	8611
Independent reflections	2791 [R(int) = 0.0425]
Completeness to theta = 24.41°	86.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2791 / 0 / 290
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1228
R indices (all data)	R1 = 0.0535, wR2 = 0.1286
Extinction coefficient	0.056(4)
Largest diff. peak and hole	0.251 and -0.242 e.$Å^{-3}$

CCDC-184219 (**4A**, **4A'**) and CCDC-181825 (**8**) contain the supplementary crystallographic data for this report. These data can be obtained free of change via www.ccdc.cam.ac.uk/conts/retrieving.html (or form the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2, 1EZ, UK; fax: (+44)1223 336 033; or deposit@ccdc.cam.uk).

REFERENCES

1. M.-E. Schwenter and P. Vogel, *Chem. Eur. J.*, 2000, **6**, 4091; M.-E. Schwenter and P. Vogel, *J. Org. Chem.*, 2001, **66**, 7869.
2. A. G. Csákÿ and P. Vogel, *Tetrahedron: Asymmetry*, 2000, **11**, 4935.
3. J. Ancerewicz and P. Vogel, *Helv. Chim. Acta*, 1996, **79**, 1393.
4. C. Marchionni, P. Vogel, and P. Roversi, *Tetrahedron Lett.*, 1996, **37**, 4149; C. Marchionni, K. Meilert, P. Vogel, and K. Schenk, *Synlett*, 2000, **8**, 1111; C. Marchionni and P. Vogel, *Helv. Chim. Acta*, 2001, **84**, 431.
5. J. Ancerewicz and P. Vogel, *Heterocycles*, 1993, **36**, 537.
6. Y. V. Il'in, V. G. Glukhovtsev, and G. I. Nikishin, *Isv. Akad. Nauk SSSR, Ser. Khim.*, 1986, **10**, 2388 (*Chem. Abstr.*, 1987, **107**, 77544).
7. C. K. Johnson, Report *ORNL-5138*, **1976**, OakBridge National Laboratory, Tenesse, USA.
8. D. A. Dougherty, K. Mislow, J. F. Blount, J. B. Wooden, and J. Jacobus, *J. Am. Chem. Soc.*, 1977, **99**, 6149, see also the structure of 1,2-cyano-1,1,2,2-tetraphenylethane: Y. Lam, G.-H. Lee, and E. Liang, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 1033.

9. J. L. Broeker, R. W. Hoffmann, and K. N. Houk, *J. Am. Chem. Soc.*, 1991, **113**, 5006; J. I. Seeman, H. V. Secor, P. J. Breen, V. H. Grassian, and E. R. Bernstein, *J. Am. Chem. Soc.*, 1989, **111**, 3140; T. Schaefer and L. B. L. Lee, *Can. J. Chem.*, 1993, **71**, 520; T. Schaefer, R. Sebastian, and G. H. Penner, *Can. J. Chem.*, 1988, **66**, 1495; J. Stokr, H. Pivcova, B. Schneider, and S. Dirlikov, *J. Mol. Struct.*, 1972, **12**, 45.
10. P. Vogel, J. Cossy, J. Plumet, and O. Arjona, *Tetrahedron*, 1999, **55**, 13521.
11. F. A. L. Anet, *Tetrahedron Lett.*, 1962, 1219.
12. P. A. Grieco, J. J. Nunes, and M. D. Gaul, *J. Am. Chem. Soc.*, 1990, **112**, 4595; W. G. Dauben, J. Y. L. Lam, and Z. R. Guo, *J. Org. Chem.*, 1996, **61**, 4816.
13. For other examples of “pincer” tandem Diels-Alder additions, see e.g.: O. Diels and K. Alder, *Ann.*, 1931, **490**, 243; O. Diels and S. J. Olsen, *J. Prakt. Chem.*, 1940, **156**, 285; C. D. Weis, *J. Org. Chem.*, 1963, **28**, 74; L. A. Paquette, M. J. Wyuret, H. C. Berk and R. E. Moerck, *J. Am. Chem. Soc.*, 1978, **100**, 5845; L. A. Paquette and D. W. Balogh, *J. Am. Chem. Soc.*, 1982, **104**, 774; R. H. Hall, S. Harkema, H. J. Den Hertog, G. L. van Hummel, and D. W. Reinhoudt, *Rec. Trav. Chim. Pays-Bas*, 1981, **100**, 312; G. Maier and W. A. Jung, *Chem. Ber.*, 1982, **115**, 804; M. Lautens and E. Fillion, *J. Org. Chem.*, 1996, **61**, 7994; M. Lautens and E. Fillion, *J. Org. Chem.*, 1998, **63**, 647; M. Lautens and E. Fillion, *J. Org. Chem.*, 1997, **62**, 4418; M. Avalos, R. Babiano, J. L. Bravo, P. Cintas, J. L. Jiménez, and J. C. Palacios, *Tetrahedron Lett.*, 1998, **39**, 9301.
14. O. Ermer, P. Bell, and S. A. Mason, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1239.
15. G. R. Jones, S. Caldarelli, and P. Vogel, *Helv. Chim. Acta*, 1997, **80**, 59; see also: D. Birney, T. K. Lim, J. H. P. Koh, B. R. Pool, and J. M. White, *J. Am. Chem. Soc.*, 2002, **124**, 5091.
16. A. A. Pinkerton, D. Schwarzenbach, J. L. Birbaum, P.-A. Carrupt, L. Schwager, and P. Vogel, *Helv. Chim. Acta*, 1984, **67**, 1136; P.-A. Carrupt and P. Vogel, *J. Mol. Struct. (Theochem)*, 1985, **124**, 9.
17. K. Kraehenbuehl, S. Picasso, and P. Vogel, *Helv. Chim. Acta*, 1998, **81**, 1439.