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Synthesis of new highly conjugated bis-(4*H*-pyrans) involving electron rich polyene linkage, by Pd° catalytic coupling of γ-methylenepyran Fischer-type carbene complexes

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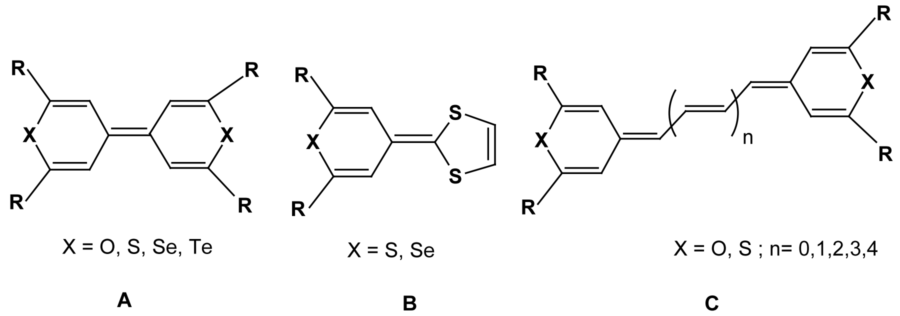
Abstract—Self dimerisation of methylenepyran carbene complexes affords bis-pyrans containing electron rich polyene linkage. The cyclic voltammograms of these new donors show one two-electron oxidation wave at low potential. © 2002 Elsevier Science Ltd. All rights reserved.

The discovery of charge transfer complex (CT) of tetrathiafulvene (TTF) and tetracyanoquinodimethane (TCNQ) as the first organic synthetic metal,[1] was the starting point of intense research in organic conductor area. A great variety of molecular structures based on the TTF framework and their group 16 analogues[2] have been synthesized in order to test the conducting,[3] superconducting[2j,3] and magnetic[4] properties of their charge-transfer complexes. Recently, their role as active chromophores for third and second order non linear optics has been evaluated.[5] Bis-(4*H*-pyrans) (BP) and chalcogenopyrans **A** (Scheme 1),[6] whose molecular properties are analogous to those of the electron donor TTF (14 π electron system of D_{2h} symmetry) have attracted less attention, because it was found that bis-thiopyran (BTP) formed a less conductive charge transfer complex with TCNQ.[7] Hybrid electron donors of TTF and BTP **B** behave similarly (Scheme 1).[2d,8]

Furthermore, conjugated and highly conjugated Δ 4,4′ bis-(4*H*-pyrans) and (thiopyrans) **C** (Scheme 1) separated by ethanediylidene groups were synthesized and the cyclic voltammograms of these donors were reported.[9] Extending the conjugation length results in coalescence of the two reversible oxidation waves (Scheme 1, **C** gives reversibly $\mathbf{C}^{+\bullet}$ and $\mathbf{C}^{+\bullet}$ gives reversibly $\mathbf{C}^{2+}$). This evolution was attributed to reduced intramolecular coulombic repulsion in $\mathbf{C}^{2+}$ as the length of the unsaturated linkage separating the pyrylium or thiopyrylium rings increases. Similar data, for extended TTF derivatives has been reported by several groups.[10]



Scheme 1.

Keywords: Fischer-type carbene complexes; bis-pyrans.

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Very recently, density functionnal calculations performed on symmetrical polyconjugated systems (β-carotene and models) indicate a localization of the two charges of the dication at the ends of the molecules. This charge localization favors the solvatation of these species providing additional stabilization.[11] Moreover, it has been found that conjugation inhibition produced by steric strain in the neutral molecules favors the oxidation and contributes to the observation of a single two-electron process.[12]

Recently, we have reported, an easy access to 'push–pull' γ-methylenepyran Ficher type carbene complexes (Scheme 2, $n=0$).[13]

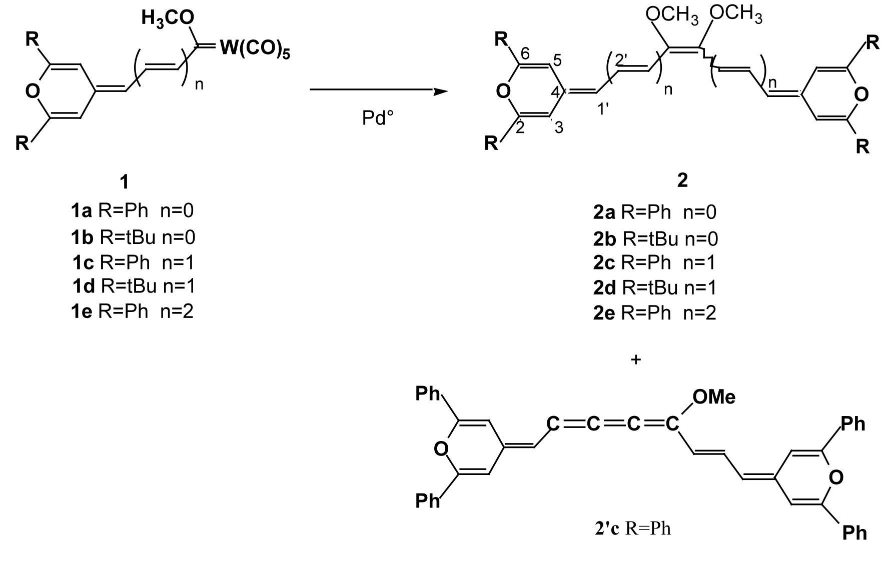
Higher vinylogues were obtained from a modified Peterson condensation between pyranylydene acetaldehyde and methyl or propenyl (methoxy)pentacarbonyl tungsten carbene complexes.[14] We anticipated, that self dimerisation of these transition metalcarbonyl stabilized carbenes would provide a convenient way to pyran nucleus separated by π electron rich polyene linkage. These highly electron rich molecules would be oxidized at low potential to form radical cations and dipyrylium cations. Since the thermal decomposition of Fischer-type carbene complexes to dimer seems to require temperatures of up to 100°C,[15] our attention was drawn by a recent study of Sierra et al. which shows that Pd° complexes are efficient catalysts for room temperature self dimerisation of aryl substituted and unsaturated Fischer-carbene complexes.[16]

At a first attempt, we carried out the dimerisation of the tungsten γ-methylene carbene complex **1a** (Scheme 2). The reaction was performed in THF at 70°C with $Pd(PPh_3)_4$ as catalyst (10% mole ratio). As expected, a rapid reaction occurred, leading to electron rich bis-pyran **2a** (68% yield, one isomer detected by 500 MHz ^{1}H NMR spectroscopy).[17] Lower yield (17%) of **2a** was obtained from the corresponding chromium carbene complex.

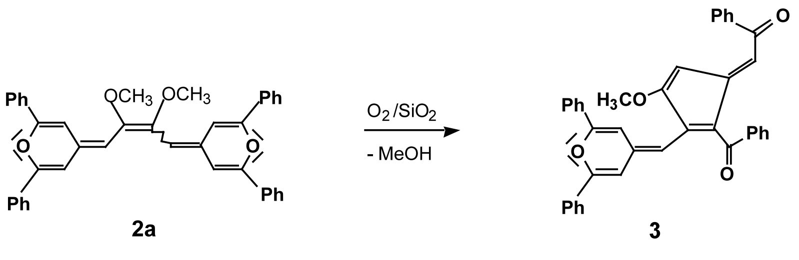
The bis-pyran **2a** is a red solid, which easily added dioxygen in CH_2Cl_2 solution in the presence of silica gel, to give by a radical process the green methylenepyran fulvene **3** (33% yield, Scheme 3).[18]

The tetratertiobutyl bis-pyran derivative **2b** was obtained similarly from the ditertiobutyl methylene–pyran Fischer-carbene complex **1b** (46% yield one isomer detected by high resolution NMR).

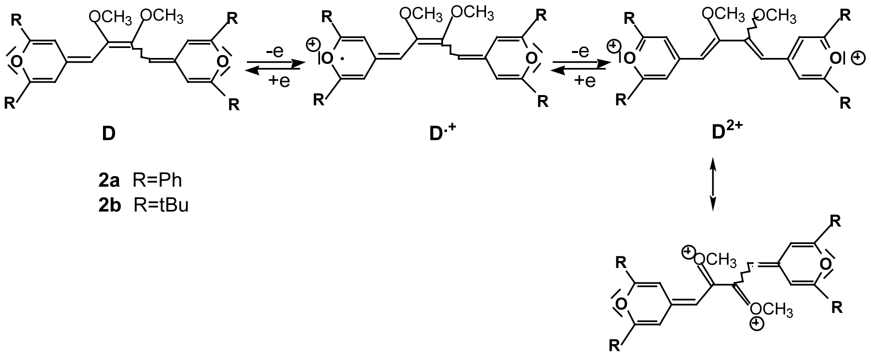
The method was exploited to synthesize higher vinylogues of **2a** and **2b**. Dimerisation of carbene **1d** and **1e** (Scheme 2) was performed using the $Pd(PPh_3)_2Cl_2$/$N(Et)_3$ system as catalyst. Bis-pyrans **2d** (two isomers (90/10%) detected by 500 MHz ^{1}H NMR) and **2e** (one isomer) were isolated in, respectively 42 and 60% yield. Under these conditions, the unsaturated carbene **1c** gives rise to an unseparable mixture of the expected bis-pyran **2c** (two isomers (90/10%)) together with a small amount of the monomethoxy cumulene product



Scheme 2.



Scheme 3.



Scheme 4.

2′c (detected by mass spectroscopy). However, pure **2c**, was attainable when the reaction was carried out using $Pd(PPh_3)_4$ as catalyst. (48% yield two isomers (90/10%)).

To study the redox properties of these new donors, voltammetric analysis was achieved on **2a** and **2b**. The cyclic voltammograms[19] of the bis-pyrans **2a** and **2b** exhibit a unique reversible two electron oxidation wave at low potential (**2a** $E° = 0.071$ V versus SCE, $\Delta E\text{p} = 0.047$ V at scan rate 0.02 V s^{-1}; **2b** $E° = 0.001$ V versus SCE, $\Delta E\text{p} = 0.049$ V at scan rate 0.10 V s^{-1}). For comparison the cyclic voltammogram of the dihydrogen bis-pyran analogue of **2a** (Scheme 1, structure **C** $n = 1$)[9a] shows two one electron reversible oxidation waves at $E_1^\circ = 0.190$ V versus SCE ($\Delta E\text{p} = 0.060$ V at scan rate 0.10 V s^{-1}) and at $E_2^\circ = 0.390$ V versus SCE ($\Delta E\text{p} = 0.060$ V at scan rate 0.10 V s^{-1}). In the series the coalescence of the two oxidation waves arises when the number of the carbons in the extended conjugation reaches eight (Scheme 1, structure **C** $n = 3$, $E° = 0.170$ V versus SCE, $\Delta E\text{p} = 0.040$ V at scan rate 0.10 V s^{-1}). It is interesting to note that this behavior results from the gradual decrease of the second oxidation potential ($\mathbf{C}^{+\bullet} \xrightarrow{-e} \mathbf{C}^{2+}$ process) as the π linker is progressively elongated

Recently, it was suggested that, in this case, charge localization at the ends of the extended dication $\mathbf{C}^{2+}$ (Scheme 1 structure **C**), associated with solvatation, which reduces the coulombic repulsion energy is responsible of the coalescence phenomenon.[11]

Assuming, as previously found for extended bis-pyrans and TTF that the oxidation sequence is a two inseparable concurrent one electron process, the difference in electrochemical behavior of **2a** and **2b** compared to **C** (Scheme 1 $n = 1$) indicates that the presence of the methoxy groups increases the donors properties of the neutral molecule **D** (Scheme 4) and stabilizes the dication state $\mathbf{D}^{2+}$ by reducing the coulombic repulsion energy.

The partial delocalization of the positive charges into the methoxy groups (Scheme 4) could reasonably explain that behavior. Conformation changes,[12] associated with the oxidation stages could also contribute to the coalescence phenomenon. To clarify this point D.F.T. calculations are currently in progress.

Extention of this study to thio, seleno, and telluro bis-pyran carbene complexes are ongoing in our laboratory. In addition, we think that new π extended TTF molecular framework would be attainable in this way, from suitable TTF Fischer-carbene complexes.

Acknowledgements

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17. All new compounds were fully characterized by IR, ^{1}H, ^{13}C or 2D NMR (HMQC, HMBC) and MS. For example: **2a** red brown solid, 88% yield; FTIR (KBr) ν (cm^{-1}): 1647, 1492, 927, 758, 687. ^{1}H NMR (CDCl$_3$, 400 MHz) 3.67 (s, 6H, OCH$_3$), 5.81 (s, 2H, H (1′), 6.41 (d, 2H, $J^4 = 1.6$ Hz, H(3)), 7.30 (d, 2H, $J^4 = 1.6$ Hz, H(5)), 7.38 (t, 4H, $J^3 = 5.7$ Hz, Ph), 7.44 (t, 8H, $J^3 = 7.2$ Hz, Ph), 7.75 (d, 4H, $J^3 = 7.3$ Hz, Ph), 7.79 (d, 4H, $J^3 = 7.3$ Hz, Ph); 2D NMR (HMBC, HMQC), (CDCl$_3$, 500 MHz) δ (^{13}C): 60.2 C(OCH$_3$), 103.9 C(5), 104.1 C(3), 109.3 C(1′), 125.0 C(Ph), 125.5 C(Ph), 129.0 C(Ph), 129.5 C(Ph), 131.0 C(4), 149.5 C(2′), 161.0 C(2), 161.0 C(6). MS m/z calcd for C$_{40}$H$_{31}$O$_4$: 575.2222 (M−H$^+$). Found 575.2228.
18. Compound **3** green solid; FTIR (KBr) ν (cm^{-1}): 2361, 1651, 1540, 1492, 1382, 1014, 941, 854, 797, 762, 688. ^{1}H NMR (THF d_8, 500 MHz, −50°C): 3.96 (s, 3H, OCH$_3$), 5.75 (s, 1H, H(1′)), 6.57 (s, 1H, H(3)), 6.65 (s, 1H, C*(H)*COPh)), 6.73 (s, 1H, H(5)), 7.25 (t, 2H, $J^3 = 7.5$ Hz, Ph), 7.39 (t, 1H, $J^3 = 7.6$ Hz, Ph), 7.44 (m, 3H, Ph), 7.54 (m, 3H, Ph), 7.58 (m, 3H, Ph), 7.62 (s, 1H, C*(H)*COCH$_3$), 7.84 (m, 6H, Ph), 8.06 (d, 2H, $J^3 = 7.3$ Hz, Ph); ^{13}C NMR (THF d_8, 500 MHz) δ: 58.3 C(OCH$_3$), 94.7 C(*C*(H)-COPh)), 105.8 C(5), 106.1 C(1′), 109.8 C(3), 118.8 C(*C*(H)COCH$_3$), 125.6 C(Ph), 125.8C(Ph), 128.9 C(Ph), 128.55 C(Ph), 129.0 C(Ph), 129.0 C(Ph), 130.0 C(Ph), 133.0 C(Ph), 140.0 C(4), 140.5 Cq, 145.8 C(2′), 152.9 C(*Cq*COPh), 153.9 C(2), 154.9 C(6), 168.8 C(*C*OCH$_3$), 190.5 C(*C*O), 194.4C(*C*O). MS m/z calcd for C$_{39}$H$_{29}$O$_4$: 561.2066 (M+H$^+$). Found 561.2067.
19. Cyclic voltammetry measurements were performed on a potentiostat EG&G 273 monitored by computer software Princeton 275, with a three-electrodes cell (platinum wire as working electrode, platinum disc as counter electrode and Ag/AgCl reference electrode, (+0.035 V versus SCE)) in dichloromethane with nBu$_4$NBF$_4$ 0.1 mol. L^{-1} as supporting electrolyte. The working electrode was polished with alumina paste, rinsed with water and ethanol, and cleaned electrochemically in H$_2$SO$_4$ (0.5 M) before each experiment.