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Reactivity of Carbanions of Fischer-Type Carbene Complexes with Pirylium Salts. Synthesis of new γ -Methylenepyran Carbene Complexes via an Addition-Oxidation-Deprotonation Process.

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Abstract : The condensation reaction between γ -unsubstituted pyrylium salts and carbanions of Fischer-type carbene complexes allowed the synthesis of new γ -methylenepyran carbene complexes. ^{13}C NMR data and single cristal X-ray analysis suggest a delocalisation of the oxygene lone pair of the heterocycle.

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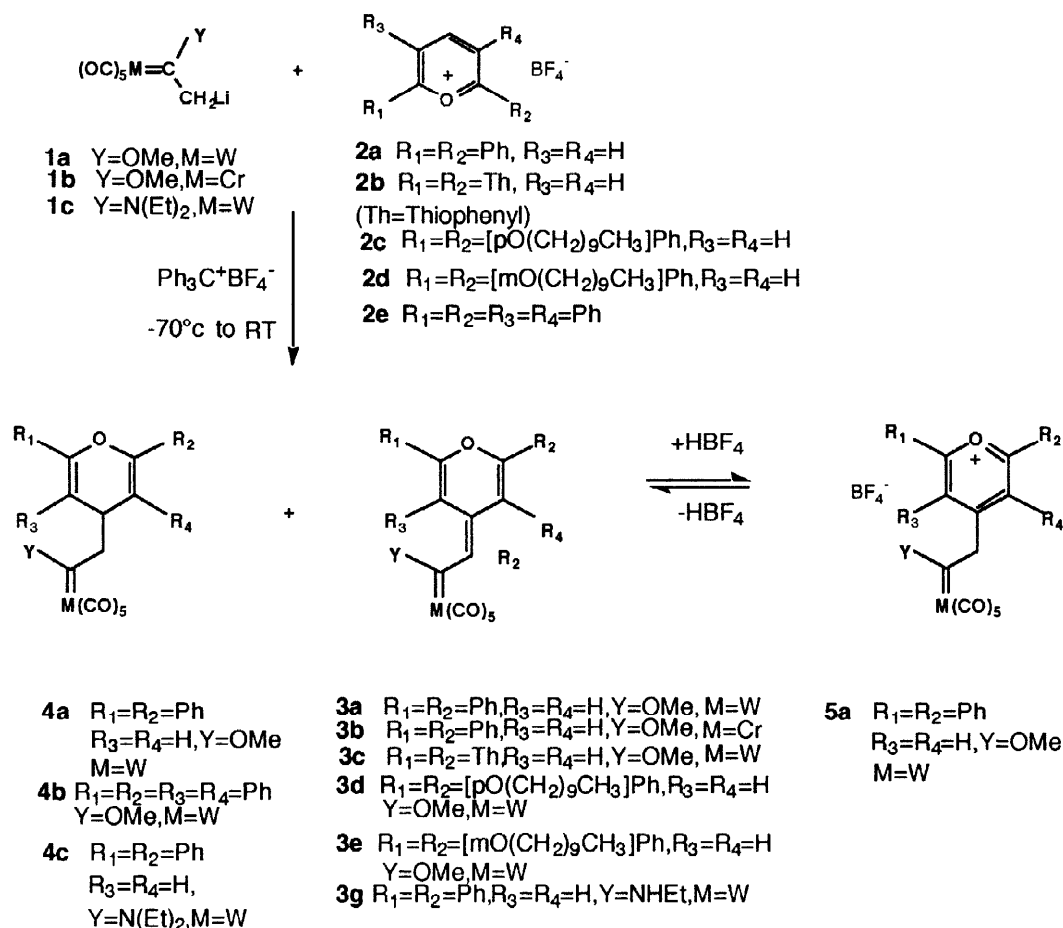
The reaction under basic conditions of γ -unsubstituted pyrylium salts with compounds possessing active methyl or methylene groups, is well documented¹. After oxidation and deprotonation, it leads to γ -methylene pyrans. As the α carbanions of Fischer-type carbene complexes are readily available², it seems likely that their condensation reaction with γ -unsubstituted pyrylium salts could provide a simple route to a new class of unsaturated carbene complexes of group 6 transition metal carbonyl³. Access to new unsaturated carbene complexes is of interest since they are widely used in organometallic⁴ and organic⁵ syntheses. In this communication, we show that the pyrylium approach allows easy formation of γ -methylenepyran⁶ bearing a metal carbonyl carbene fragment.

Carbanion **1a** (scheme 1), generated from n-butyllithium and the corresponding Fischer-type carbene complex, was reacted with 2,6-diphenyltetrafluoroborate pyrylium salt **2a**. After chromatography, deep purple γ -methylenepyran complex **3a** (43% yield) was obtained. A small quantity of yellow pyran complex **4a** (13% yield) also formed. Using two equivalents of **2a**, and adding triphenylcarbenium tetrafluoroborate salt to the reaction mixture, led to **3a** being the sole isolated product (85% yield)⁷.

According to previous studies¹, the formation of **3a** was the result of **4a** oxidation by the excess of **2a**, or more efficiently by the triphenylcarbenium tetrafluoroborate salt. The pyrylium salt **5a** obtained, deprotonates as soon as it forms, leading to **3a**. It is worth noting that 1) the pyran **4a** was also slowly oxidized to **3a** by dioxygen in diethylether solution or in a solid state incorporated into a thin layer chromatography plate. 2) the intermediate pyrylium salt **5a** could be obtained in the form of a yellow precipitate by adding HBF_4 to a solution of **3a** in CH_2Cl_2 (scheme 1).

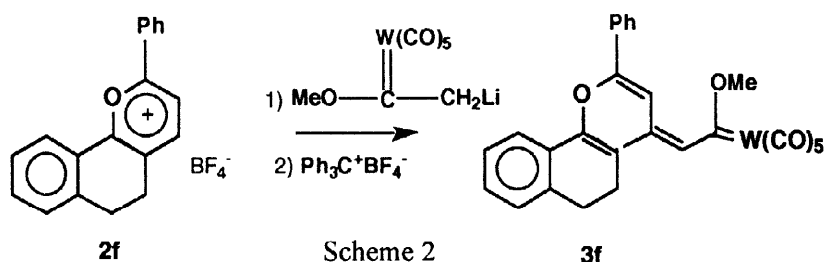
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The reaction of pyrylium salt **2a** with carbanion **1b** of the chromium carbene complex proceeded similarly to afford chromium carbene γ -methylene-pyran complex **3b** in 55% yield (scheme 1).



Scheme 1

The reaction was extended, without any modification, to 2,6-dithiophenylpyrylium salt **2b** and to 2,6-diarylpyrylium salts **2c** and **2d** which are known to exhibit a thermotropic liquid crystalline behaviour⁸. γ -methylene-pyran complexes **3c**, **3d** and **3e** were obtained in moderate yield (25, 20 and 30% respectively). Finally the reaction of fused ring pyrylium salts **2f** with carbanion **1a** afforded the expected tricyclic γ -methylene-pyran complex **3f** in 54% yield (scheme 2). On the other hand, when carbanion **1a** was opposed to 2,3,5,6-tetraphenylpyrylium salt **2e**, the reaction, perhaps for steric reasons, stopped at the pyran stage (obtention of **4b**, 40% yield ; scheme 1).



Scheme 2

We examined then the action of carbanion of the diethylaminocarbene complex **1c**. Thus, treating pyrylium salt **2a** with carbanion **1c** followed by the addition of trityl salt gave the yellow pyran complex **4c** in 43% yield. In this case, the formation of the aminocarbene γ -methylenepyran complex analogous to **3a** did not occur⁹. However, the substitution from **3a** of the methoxy group by an ethylamino group³, provided easy access to the expected ethylamino unsaturated carbene complex **3g**¹⁰ (37% yield ; scheme 1). The transformation performed using diethylamine was unsuccessful.

The structure assignment of new methylenepyran complexes is based on ¹H, ¹³C NMR data and X-ray structure analyses of **3f**¹¹. Compounds **3a-3f** can be described by the two extreme resonance methylenepyran A and pyrylium B structures¹² (scheme 3). The colour of complexes **3a-3f** (deep purple) together with the high field ¹³C resonance of the carbenic carbon atom of **3a**¹³ ($\delta = 284$ ppm) indicate a delocalisation of the oxygen lone pair of the pyran ring¹⁴. Single crystal X-ray analysis of **3f** (Figure 1) gave complementary information relating to the pyran-pyrylium characters of these complexes.

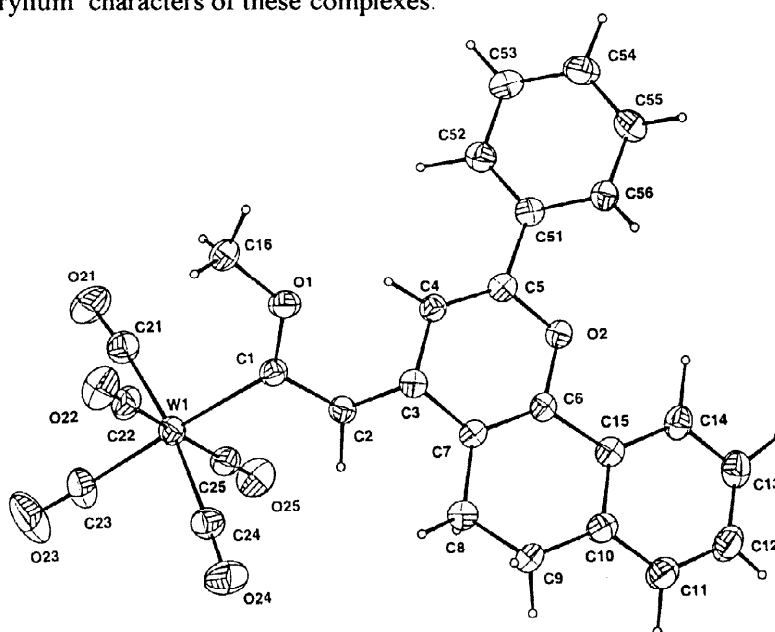
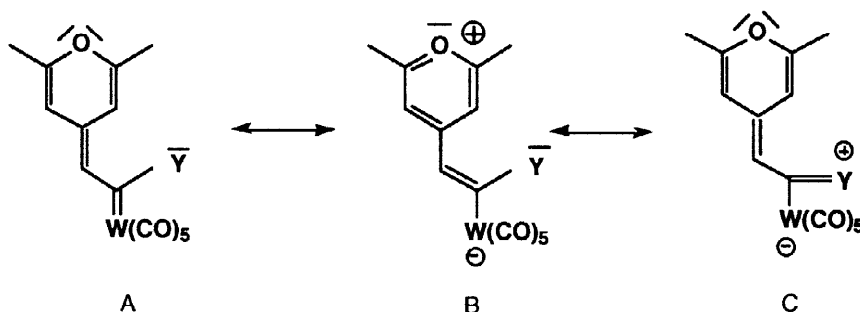


Figure 1: ORTEP drawing of complex **3f**.

Selected bond distances Å: W-C1, 2.218 (7); C1-O1, 1.318 (9); C1-C2, 1.43 (1); C2-C3, 1.40 (1); C3-C4, 1.44 (1); C4-C5, 1.33 (1); C5-O2, 1.346 (8); C6-O2, 1.372 (9); C6-C7, 1.36 (1); C7-C3, 1.43 (1). Bond angles (°): W1-C1-O1, 130.0 (6); W1-C1-C2, 120.1 (5); C2-C1-O1, 109.9 (7); C1-C2-C3, 131.2 (7); C2-C3-C4, 124.3 (7); C2-C3-C7, 120.3 (6); C4-C3-C7, 115.2 (6); C3-C4-C5, 121.2 (7); C4-C5-O2, 122.4 (6); C5-O2-C6, 119.0 (5); O2-C6-C7, 122.2 (6); C6-C7-C3, 119.9 (6).

The W-C (carbene) distance (2.218 Å) proves to be significantly longer than the W=C distance found in the (CO)₅W=C(OMe)Ph complex (2.05 Å)¹⁵. This value suggests some contribution of the resonance structure B (scheme 3). In addition, the alternating bond distance pattern between the carbon atoms of the heterocycle is not much different from that found in pyrylium salts substituted in the γ position by *p*-dimethylaminophenyl¹⁶ or cymentrenyl¹⁷ electron donating groups. In these salts the pyran resonance structure significantly contributes to the valence bond description¹⁶. However, the C1-C2, C2-C3 bond distances (1.43 and 1.40 Å) reveal that the contribution of the pyran resonance structure A remains important. Finally, the

colour of the ethylamino carbene complex **3g** (yellow), together with the ^{13}C NMR resonance of the carbenic carbon ($\delta = 242$ ppm) which is close to those found in the non-oxygenated unsaturated complexes³ suggests that, in this case, the pyrylium character is less developed as a consequence of the delocalisation of nitrogen lone pair (scheme 3C).



Scheme 3

The reactivity of these new unsaturated carbene complexes is under study.

Reference and notes

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To a solution of methoxymethylpentacarbonylcarbene complex ($1.6 \cdot 10^{-3}$ mol) in dry THF (10 ml) under N_2 atmosphere, 0,75 ml ($1.6 \cdot 10^{-3}$ mol) of a 2,1 M solution of n-butyllithium was added at -78°C . Pyrylium salt ($3.2 \cdot 10^{-3}$ mol) was then added. The solution was stirred during 1 hour at room temperature. Removal of the THF at low pressure left a deep purple residue which was diluted in 20 ml of CH_2Cl_2 . Triphenylcarbenium salt was then added. Removal of the solvent left a residue which was subjected to column chromatography on kieselgel (0,063-0,200 mm) employing 20:80 v/v petroleum ether-diethyl ether as eluent. Methylenepyrans was isolated and recrystallized from diethyl ether.
selected spectrographic data; methylenepyrans **3f**; FTIR ν (cm^{-1}): 2053.7, 1967.6, 1899.3, 1631.9, 1575.9, 1481.9, 1216.8; Mass spectrum: m/z calcd. 638.0567; m/z found 638.0585; NMR ^1H (acetone d_6) δ (ppm), 2.85 (t, 2H, $J_{\text{HH}} = 7.86\text{Hz}$); 3.05 (t, 2H, $J_{\text{HH}} = 7.94\text{Hz}$); 4.55 (s, 3H); 7.1 (s, 1H); 7.4 (m, 2H); 7.54 (m, 4H); 7.87 (m, 4H) 8.14 (s, 1H); NMR ^{13}C (acetone d_6) δ (ppm), 21.973 (t, $J_{\text{CH}} = 124.86\text{Hz}$); 26.909 (t, $J_{\text{CH}} = 117.8\text{Hz}$); 67.886 (q, $J_{\text{CH}} = 145.23\text{Hz}$); 107.841 (d, $J_{\text{CH}} = 177.1\text{Hz}$); 117.001 (s); 122.976 (d, $J_{\text{CH}} = 159.5\text{Hz}$); 125.719 (s); 127.221 (d, $J_{\text{CH}} = 154.9\text{Hz}$); 128.039 (d, $J_{\text{CH}} = 159.4\text{Hz}$); 128.380 (s); 129.235 (d, $J_{\text{CH}} = 160\text{Hz}$); 130.881 (d, $J_{\text{CH}} = 160\text{Hz}$); 131.132 (d, $J_{\text{CH}} = 160\text{Hz}$); 132.142 (s); 136.718(s); 137.841 (s); 155.763 (s); 158.945 (s); 199.258 (s); 204.93 (s); 286.072 (s).
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- Complementary works will be necessary to find the origin of this lack of reactivity.
- Only one isomer could be detected: methylenepyrans **4c**; FTIR ν (cm^{-1}): 2055.4, 1897.5, 1654.2, 1516.1; Mass spectrum: m/z calcd. 625.0722; m/z found. 625.0731; NMR ^1H (acetone d_6) δ (ppm), 1.56 (t, 3H, $J_{\text{HH}} = 7,24\text{Hz}$); 4.01 (m, 2H, $J_{\text{HH}} = 6,05\text{Hz}$); 6.44 (s, 1H); 6.74(dd, 1H, $J_{\text{HH}} = 1.96\text{Hz}$, $J_{\text{HH}} = 0.68\text{Hz}$); 6.75 (d, 1H, $J_{\text{HH}} = 1.81\text{Hz}$); 7.4-7.6 (m, 6H); 7.8-8 (m, 4H); 10,4 (s, 1H).
- Crystal data: $\text{C}_{27}\text{H}_{18}\text{O}_7\text{W}$, FW = 638,3, monoclinic, space group $\text{P}2_1/\text{C}$, $a = 7,442$ (4), $b = 24,256$ (4), $c = 13,324$ (3) Å, $\alpha = 90^\circ$, $\beta = 97,71^\circ$ (3), $\gamma = 90^\circ$, $v(\text{\AA}^3) = 2384$ (1), $Z = 4$, $D_c = 1,78\text{g}/\text{cm}^3$, $\text{MoK}\alpha$ radiation ($\lambda = 0,71069\text{\AA}$).
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