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Reaction of carbanion of Fischer-type carbene complexes with pyrylium salts. One pot substituted benzophenones formation by subsequent cyclization and double hydrogen β-elimination

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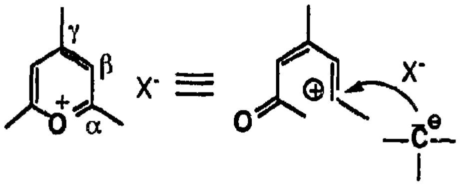
Abstract

Carbanions of Fischer-type carbene complex react with pyrylium salts. The unstable dienone formed gives substituted benzophenones after ring-closure and aromatization by double hydrogen β-elimination. © 1997 Elsevier Science S.A.

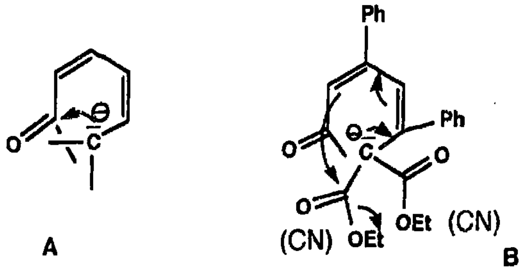
Keywords: Tungsten carbene complexes; Pyrylium salts

1. Introduction

Addition of carbanions to pyrylium salts, which act as pentadienone cation equivalents [1] (Scheme 1), is a convenient method for carbon–carbon bond formation. This method has not only been applied to the stereoselective synthesis of natural acyclic products such as leukotriene and retinal analogues [2–4] but also to the construction of a benzenic nucleus [1]. This formation requires an intramolecular cyclization in the basic medium. In almost all cases, it implies a reaction between the incoming anionic carbon atom and the carbonyl function produced by the pyrylium ring opening [5–8] (Scheme 2**A**). Special cases are the reaction of the malonitrile and malonate anions with 2,4,6-triphenylpyrylium salts [9]. Following the addition of carbanion to the pyrylium ring, a cyclization step occurs, involving the electrophilic carbon of the nitrile or ester function borne by the incoming carbanion. In these examples two carbon atoms of the nucleophile are incorporated into the formed benzene ring (Scheme 2**B**). In this communication is reported for the first time the addition of stabilized metal carbonyl carbanions to pyrylium salts. It is shown that carbanions of Fischer-type carbene complexes [10] add to the 2,4,6-substituted triphenylpyrylium salts at the α-carbon atom of the heterocycle (Scheme 1). The dienone obtained gives highly substituted benzophenones after ring closure and aromatization.



Scheme 1.



Scheme 2.

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2. Results and discussion

The carbanion **2a** (Scheme 3, M = W), prepared by the action of *n*-butyllithium on the Fischer-type carbene complex **1** reacts with the 2,4,6-triphenylpyrylium tetrafluoroborate salt **3a** to give the benzophenone **4a** in a fair yield (47% of isolated recrystallized product). The reaction induced using two equivalents of BuLi does not enhance the yield. A similar result is obtained using the carbanion of the chromium carbonyl carbene complex **2b** (Scheme 3, M = Cr). In this case the benzophenone **4a** is formed in lower yield (23%). The same reaction is observed with the pyrylium salts **3e**, **3b**, **3c** and **3d** bearing electron-withdrawing and electron-donating groups (30–40% yield). [1]

In all cases, unreacted pyrylium salts and their pseudobases are recovered, and the presence of tungsten hexacarbonyl in the reaction mixture is detected by IR and mass spectroscopy. [2] Finally, the carbanion **5** of the amino Fischer-type carbene complex (Scheme 4) slightly reacts with the 2,4,6-triphenylpyrylium tetrafluoroborate salt to give the carbene complex **6** (20% yield after chromatography). In this case no cyclization product could be detected and a great part of the pyrylium salt pseudobase is recovered.

The above results suggest the possible mechanistic paths outlined in Scheme 5: Adding carbanion to the α-electrophilic carbon atom of the heterocycle followed by ring opening, results in unstable methoxy Fischer carbene with a pendent dienone [11]. The formation of the unsaturated six carbon atoms ring from A can occur along two different paths leading either to the zwitterion B [3] [14] or to the fused ring metallacyclobutane C [15,16]. According to previous studies [11] relevant to the mechanism of the intramolecular cyclopropanation reactions, the last reaction pathway would require in the first step the formation of a chelated η^2-dienone complex.

In the both cases, the cyclization step is favoured by the proximity of carbon 2 and the carbenic carbon, which implies an *E* stereochemistry around the C4=C5 double bond. Finally the zwitterion B or the metallacyclobutane C gives the benzenic ring by a double hydrogen β-elimination process. [4]

The lack of aminobenzophenone formation from C may be due to the steric requirement of the diethylamino group but also to other factors. For intramolecular cyclopropanation reactions, it has been previously reported that the amino carbene complexes are much less reactive. [5]

We have shown that combining Fischer-type carbene complexes with pyrylium salts chemistry allows the formation of a benzenic nucleus, in which the organic part of the initial organometallic carbene is incorporated. The reaction described here is a new (C2 + C4) transformation [1] of pyrylium salts. Further studies on 2,6- and 2,4-substituted pyrylium salts are under way.

3. Experimental details

3.1. General procedure for the preparation of benzophenones.

0.75 ml (1.87×10^{-3} mol) of *n*-butyllithium (2.5 M) at −78°C under N_2 was added to a solution of the carbene complex **1a** (600 mg, 1.6×10^{-3} mol) in 10 ml of dry THF. The solution was stirred for 15 min. 2,4,6-triphenylpyrylium salt **3a** (759 mg, 1.92×10^{-3} mol) was then introduced at −78°C. The solution was stirred for 30 min at −78°C and then for 2 h at room temperature. THF was then removed under reduced pressure. The benzophenone **4a** was isolated by recrystallization in methanol (273 mg, 7.52×10^{-4} mol, 47% based on the carbene complex).

3.2. Selected spectrographic data

Benzophenone **4a**: mp 156°C; IR (KBr) cm^{-1} : 1672w, 1597w, 1561w, 1266w; mass spectrum calcd for $C_{26}H_{20}O_2$ *m/e* 365.1542, found *m/e* 365.1545; ^1H NMR (acetone-d_6) δ ppm: 4.86 (s, 3H), 7.25–7.55 (m, 9H), 7.7–7.9 (m, 3H); ^{13}C NMR (acetone-d_6) δ ppm: 56.42 (q, $J^1_{CH} = 144$ Hz), 109.8 (dd, $J^1_{CH} = 159$ Hz, $J^3_{CH} = 6.6$ Hz) 121.8 (dd, $J^1_{CH} = 161$ Hz, $J^3_{CH} = 6$ Hz), 128.1 (d, $J^1_{CH} = 159$ Hz), 128.2 (d, $J^1_{CH} = 160$ Hz), 128.3(s), 128.8 (d, $J^1_{CH} = 159$ Hz), 128.9 (d, $J^1_{CH} = 159$ Hz), 129.5 (d, $J^1_{CH} = 159$ Hz), 130.8 (d, $J^1_{CH} = 158$ Hz), 130.85 (d, $J^1_{CH} = 160$ Hz), 130.9 (d, $J^1_{CH} = 159$ Hz), 134 (dt, $J^1_{CH} = 161$ Hz, $J^3_{CH} = 7.4$ Hz), 139 (t, $J^3_{CH} = 7.4$ Hz), 140.8(s), 141.2(s), 142.5(s), 144(s), 158.4(s), 192.2(s).

Carbene **6**: mp 110°C; IR (KBr) cm^{-1}: 2060m, 1910w, 1878w, 1648m, 1447m, 1218m; mass spectrum calcd for $C_{34}H_{29}NO_6W$ *m/e* 729.1476, found *m/e*

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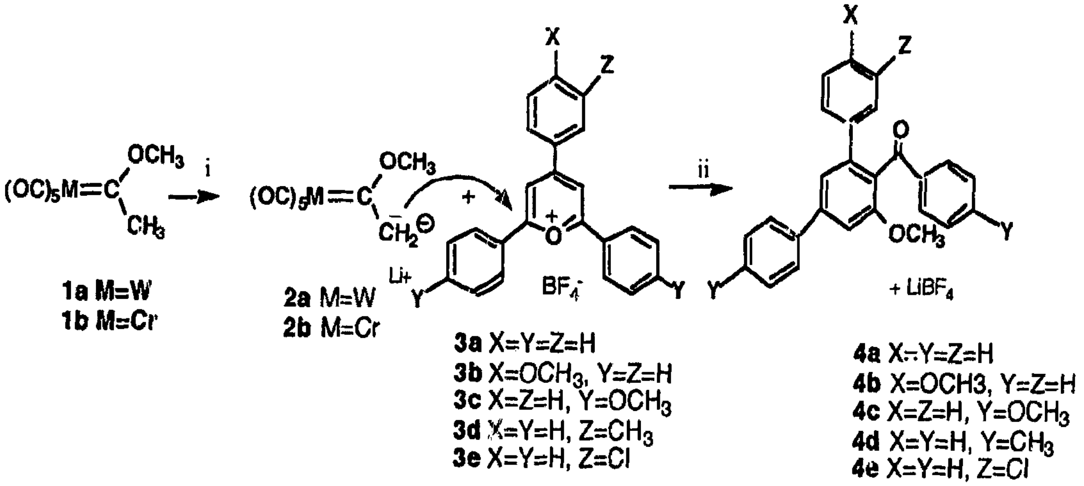
[1] All compounds have been fully characterized using ^{13}C and ^1H NMR, IR and mass spectroscopy.

[2] Several other uncharacterized by-products are detected by thin layer chromatography.

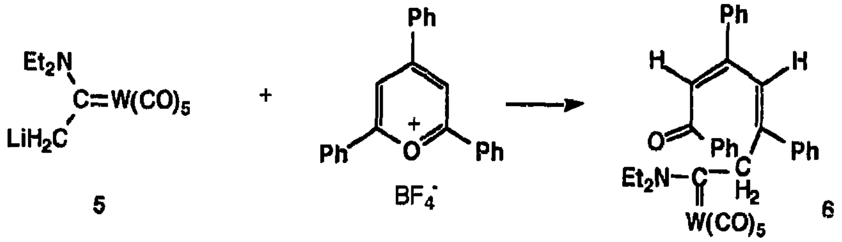
[3] It is well established that the carbon 2 of a dienone has the greatest atomic coefficient in the highest occupied molecular orbital (HOMO) [12]. M.O. calculations on the methoxy carbene complex **1b** show that the lowest unoccupied molecular orbital (LUMO) is mostly localized on the carbene carbon atom [13].

[4] A similar type of evolution has been suggested to explain the unexpected formation of dihydropyran derivatives from a metallacyclobutane intermediate [16].

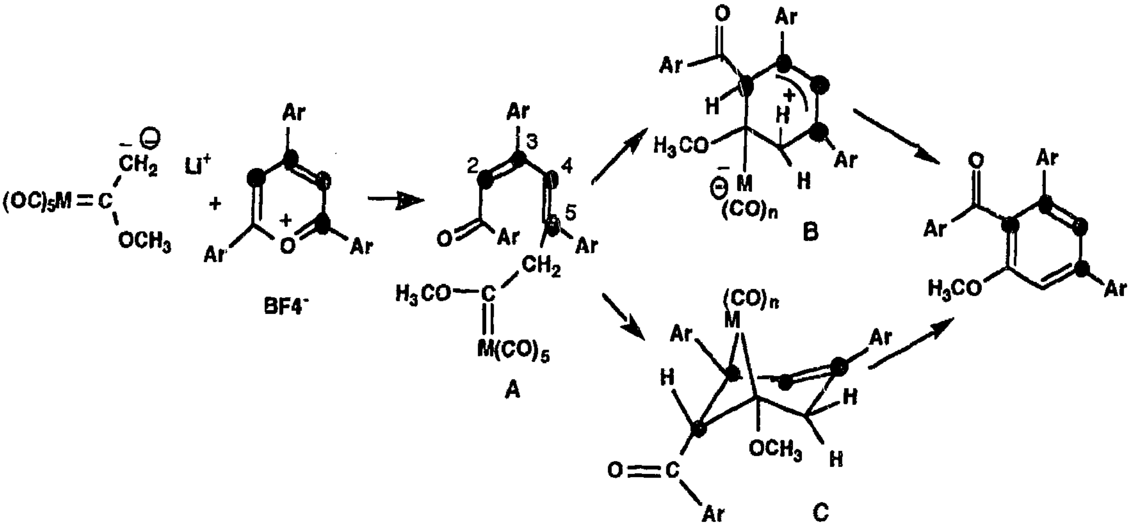
[5] See for example, Ref. [16]. In this work, it is reported that an alkoxy carbene complex with a pendent olefin reacts below 0°C and the amino carbene analogue at 140°C.



Scheme 3.



Scheme 4.



Scheme 5.

729.148; ^{1}H NMR (acetone-d_6) δ ppm: 1.45 (t, 3H), 1.62 (t, 3H), 4.2 (q, 2H), 4.5 (q, 2H), 4.55 (d, 2H, $J^4 = 1.7$ Hz), 6.7 (m, 1H, $J^4 = 1.52$ Hz, $J^4 = 1.8$ Hz), 7.2 (d, 1H, $J^4 = 1.5$ Hz) 7.1–7.6 (m, 15H), 8.05 (d, 2H); ^{13}C NMR (acetone-$d6$) δ ppm: 14.7 (q, $J^1_{CH} = 157$ Hz), 14.8 (q, $J^1_{CH} = 158$ Hz), 47.7 (t, $J^1_{CH} = 154$ Hz), 60.3 (t, $J^1_{CH} = 154$ Hz), 60.8 (t, $J^1_{CH} = 155$ Hz), 127.8–129.8 (m), 133 (dt, $J^1_{CH} = 160$ Hz, $J^3_{CH} = 8.1$ Hz), 140(s), 141.2(s), 141.5(s), 142.2(s), 155(s), 190(s), 199(s), 204.2(s), 251.4(s).

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