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Scandium Trifluoromethanesulphonate as an Active Catalyst in the Decarbonylation of Aromatic Aldehydes [+]

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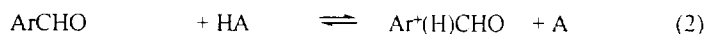
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Abstract: Scandium trifluoromethanesulphonate efficiently catalyzes the decarbonylation of 2,4,6-trimethoxybenzaldehyde (1) which, on heating in MeOH solution, is deformylated neatly and completely in a few minutes, yielding 1,3,5 trimethoxybenzene and methyl formate. The reaction was studied by UV and NMR spectroscopy, which gave evidence for the reaction mechanism. Aromatic aldehydes less electron rich than 1 were decarbonylated more sluggishly. The unique catalytic properties of Sc(OTf)3 were compared with other non transition metal triflates. Copyright © 1996 Elsevier Science Ltd

The hard character, high coordination numbers and high affinity toward carbonyl oxygen make lanthanide compounds valuable catalysts in several organic reactions, including some important carbon-carbon forming processes.[1,2] This catalytic activity is generally referred to as a Lewis acid like behaviour of the lanthanide salts; however, a detailed study of the mechanism of these reactions, as well as the characterization of the possible intermediates, is usually lacking. Recently, lanthanide triflates, especially $Yb(OTf)_3$ and $Sc(OTf)_3$, were reported to be good catalysts for the Fries rearrangement [3] and the Friedel-Crafts acylation of aromatic substrates. [4] The latter reaction, when catalyzed by proton or Lewis acid catalysts has generally been considered to be irreversible, even if there is a number of instances of electrofugal acyl groups in the presence of concentrated mineral acids.[5] Since several proton and lanthanide catalyzed reactions follow similar mechanisms, it was therefore interesting to investigate the behaviour of aromatic aldehydes and ketones on exposure to lanthanide salts. Indeed, one could anticipate that the coordination with the lanthanide ion would enhance the electrofugacity of the carbonyl group, thus facilitating the deacylation reaction, especially if the ordinary arenium ion mechanism is involved.[6]

In this paper we describe the facile decarbonylation of some electron-rich aromatic aldehydes in the presence of $Sc(OTf)_3$.[7] At first, we investigated in detail the reaction of 2, 4, 6-trimethoxybenzaldehyde (1) whose decarbonylation in aqueous mineral acid media (HA) was shown to follow the general acid-base mechanism of successive bimolecular proton transfer steps.[8]

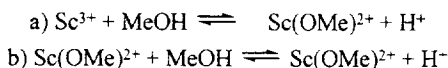[+] Dedicated to Professor Paolo Grunanger on the occasion of his 70th birthday.

$$\text{ArCHO} \quad + \text{HA} \quad \rightleftharpoons \quad \text{ArCHO}^+\text{H} \quad + \text{A} \qquad (1)$$

$$\text{ArCHO} \quad + \text{HA} \quad \rightleftharpoons \quad \text{Ar}^+\text{(H)CHO} \quad + \text{A} \qquad (2)$$

$$\text{Ar}^+\text{(H)CHO} \quad + \text{A} \quad \rightleftharpoons \quad \text{ArH} \quad + \text{HCOA} \qquad (3)$$

Kinetic studies indicated that a single protonation takes part in the acid catalysis and that the oxygen conjugate acid ArCHOH$^+$ (eq 1) probably is not involved directly in the decarbonylation of **1**; instead, the second (eq 2) or third step (eq 3) is rate controlling.[8]

Results and Discussion

After long experimentation we found that 2,4,6-trimethoxybenzaldehyde (**1**) (0.13 M) was nicely decarbonylated upon exposure to Sc(OTf)$_3$ in MeOH. With 0.16 equiv of scandium triflate the reaction went to completion in 6 hours at 25 ° C and in only 15 min in MeOH at reflux, while with 1 equiv of the catalyst complete reaction took place in less than 10 min on heating in MeOH solution. In all of these runs we identified 1,3,5-trimethoxybenzene (mp 51-53°C) and HCO$_2$Me as the only reaction products.[9]

Notwithstanding striking similarities between the Sc^{3+} and the mineral acid catalysed [8] decarbonylation reaction of **1**, the catalytic activity of Sc(OTf)$_3$ could not be ascribed entirely to the enhanced proticity of MeOH. Potentiometric titration clearly indicated that Sc(OTf)$_3$ in MeOH solution gave rise to two equilibria :

$$\text{a) Sc}^{3+} + \text{MeOH} \rightleftharpoons \text{Sc(OMe)}^{2+} + \text{H}^+$$

$$\text{b) Sc(OMe)}^{2+} + \text{MeOH} \rightleftharpoons \text{Sc(OMe)}^{2+} + \text{H}^-$$

whose constants, determined by the program SUPERQUAD, are: a) pK$_1$=5.35; b) pK$_2$= 6.12 (details will be published elsewhere). However,two 0.13 M methanolic solutions of Sc(OTf)$_3$ and TfOH showed comparable catalytic activity, notwithstanding the former was more than 100 times less acidic than the latter. On the other hand, of two methanolic solutions of TfOH and Sc(OTf)$_3$ having comparable acidity, only the latter accelerated the decarbonylation of **1**. These results clearly indicated that a specific interaction of the aldehyde carbonyl group with Sc^{3+} salt was involved in the decarbonylation; however, the mechanism of the reaction was different from that followed in strong acidic media (see above). Evidence was obtained from the UV and NMR spectra of **1** in the presence of Sc(OTf)$_3$.

At first, the UV spectra of **1** were determined in an aprotic solvent like MeCN. On addition of Sc(OTf)$_3$. the ^1L_a band showed a marked bathocromic shift from 284 (ε= 16595) to 326 nm (ε= 40000), accompanied by a notable increase in the absorption intensity (Fig. 1). These spectral changes were very similar to the ultraviolet changes observed for **1** in various strengths of aqueous HClO$_4$ where the conjugate acid ArCHOH$^+$ was formed (equation 1).[8] Therefore, they corresponded to the equilibrium between **1** and the complex **2** and indicated a stabilization of the planar zwitterionic species **2b** and **2c** due to

complexation with Sc^{3+} (equation 4).[10] Apparently, internal chelation of Sc^{3+} with o-methoxyl groups could exert an additional stabilization of complex **2** compared to the free aldehyde **1**.

In accordance with the formation of complex **2**, the ^{1}H-NMR spectra of **1** in MeCN-d_3 showed that the formyl proton experienced a downfield shift on increasing concentration of $Sc(OTf)_3$; by contrast, the
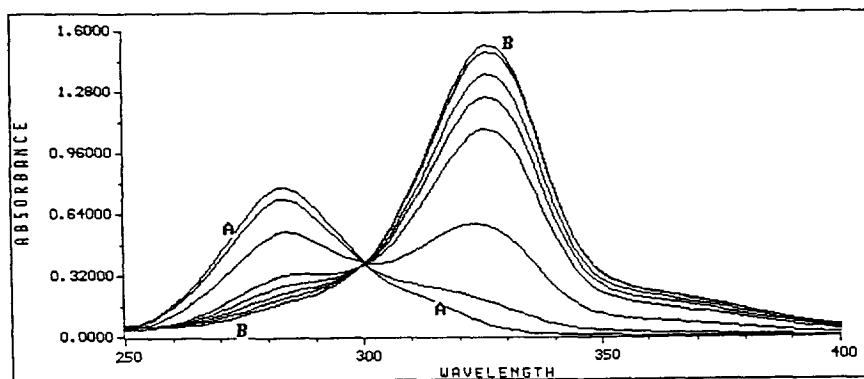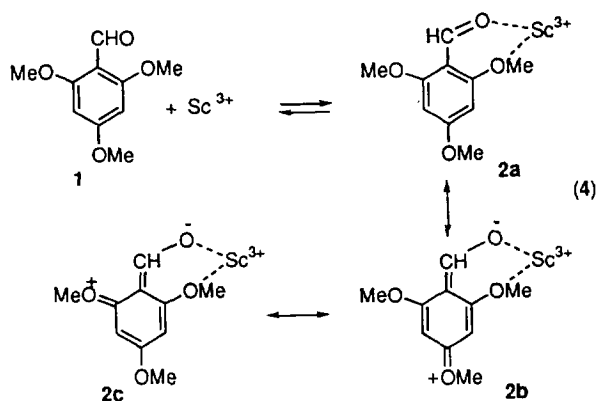

Fig. 1. UV spectra of the system 2,4,6-trimethoxybenzaldehyde - scandium triflate in MeCN solution. A, 2,4,6-trimethoxybenzaldehyde 4.292×10^{-5} mol; B, molar ratio of 2,4,6-trimethoxybenzaldehyde - scandium triflate = 1 : 150; intermediate spectra, molar ratios = 1 : 10, 1 : 20, 1 : 40, 1 : 60, 1 : 80, 1 : 100

(4)

chemical shifts of the aromatic and OCH_3 protons were not significantly affected,[11] pointing out that the added Sc^{3+} ion was bound to the carbonyl oxygen of **1** more strongly than to the ortho ether oxygens. The stoichiometry of complex **2** was established to be 1:1 by the continuous variation method,[12] whereas the pk_f value, determined by the Benesi-Hildebrand-Scott method [13] was -2.75 ± 0.05.[14, 15]

Then, we determined the UV spectra of the system 1-Sc(OTf)₃ in MeOH solution at 25 C. (Fig 2). Not surprisingly, these spectra were significantly different from those obtained in MeCN, since the ¹Lₐ band at 288 nm suffered a remarkable decrease in intensity without being shifted to a longer wavelength; instead, the benzenoid band at 228 nm showed a marked increase in the absorption intensity.[10] These changes clearly indicated that addition of Sc(OTf)₃ to 1 in MeOH solution caused a decreased conjugation of the aromatic ring to the carbonyl group giving rise to complexes different from those observed in MeCN.[16] Indeed, we believe that various ternary complexes of general formula 1-Sc³⁺-(MeOH)ₙ (3) are readily formed in MeOH (Scheme 1), because of the high oxophilicity and coordinating power of the Sc³⁺ ion which should be in MeOH as effective as in MeCN.[17] The carbonyl group in complex 3 is obviously activated[18] towards the attack of a nucleophilic MeOH molecule which, on the other hand, being coordinated to the same Sc³⁺ ion as the carbonyl group, should give rise to a fast addition reaction.

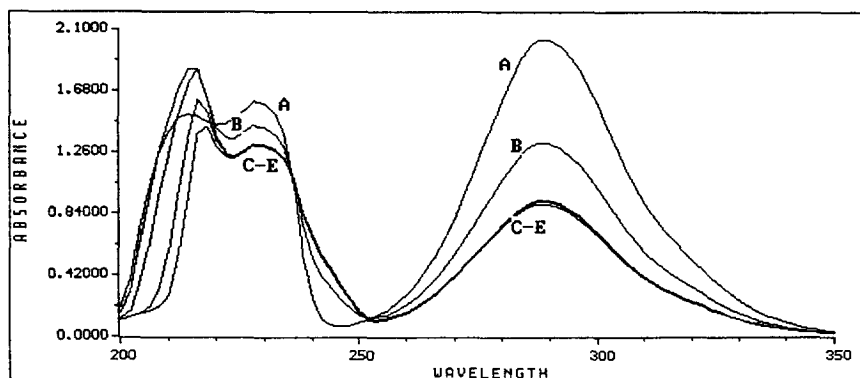The observed ultraviolet changes (Fig. 2) were thus due to an equilibrium between 3 and the corresponding

Fig. 2 . UV spectra of the system 2,4,6-trimethoxybenzaldehyde - scandium triflate in methanol. A, 2,4,6-trimethoxybenzaldehyde 1.04 x 10⁻⁴ mol; B, molar ratio of 2,4,6-trimethoxybenzaldehyde - scandium triflate = 1 : 1; C, D, E molar ratios = 1 : 10, 1 : 50, 1 : 100. C, D, E curves are superimposed

hemiacetal species 4 and 5 which no longer contained a conjugated carbonyl group.[19] Moreover, these same hemiacetals are likely intermediates in the decarbonylation reaction of 1, being advanced precursors to 1,3,5-trimethoxybenzene.

In fact, there is no reason why the rather acidic hemiacetal proton[20] in 5 cannot readily be transferred intramolecularly to the ipso position of the highly electron-rich aromatic ring which., contrary to 1, is not deactivated by conjugation with the formyl group. The aromatic sextet is then restored from the Wheland complex 6 via displacement of HCO₂Me to afford 1,3,5-trimethoxybenzene.[21]

In conclusion, in the mechanism proposed for this new catalyzed protiodecarbonylation of 1 (Scheme 1) the Sc³⁺ ion exerts a template effect coordinating and thus activating both partners of the reaction, i.e.
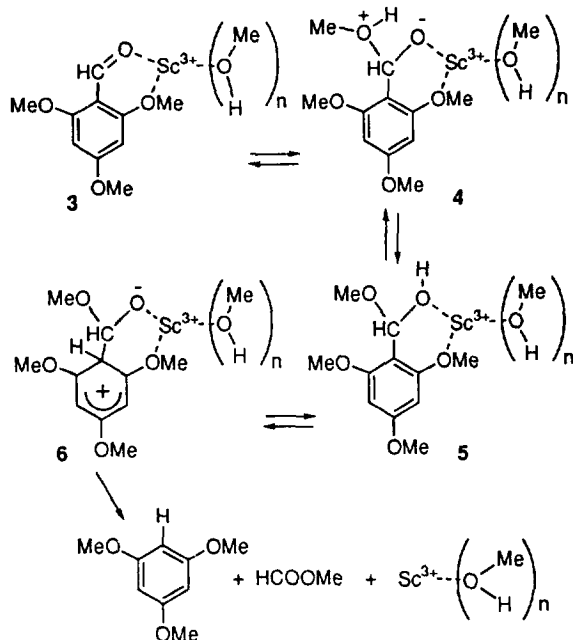
Scheme 1. Mechanism proposed for the Sc(OTf)₃ catalyzed decarbonylation of 2,4,6-trimethoxy-benzaldehyde (1) in MeOH solution.

aldehyde 1 and MeOH.

Addition of Sc(OTf)₃ (0.16 equiv) to aldehyde 1 in MeOH-d_4 solution led to establishment of rapid equilibria which caused a considerable broadening of the ^{1}HNMR signals, thus precluding kinetic studies and a sure identification of the postulated reaction intermediates. However, extending our studies to the decarbonylation of other aromatic aldehydes we obtained firm evidence for the intermediacy of hemiacetals like 5 and 6 . Contrary to 1, the decarbonylation of 3-formylchromone (7) could easily be followed by NMR spectroscopy. Shortly after addition of Sc(OTf)₃ (0.16 equiv.) to 7 in MeOH-d_4 solution at 25 °C, the NMR spectrum showed, instead of the signals of free 3-formylchromone, those of the corresponding O-methyl hemiacetal and O,O-dimethyl acetal whose singlets at δ 5.95 and 5.55 ppm were highly diagnostic.[2a] On heating the solution at 60 °C the intensity of these signals slowly decreased while other signals assignable to chromone (8) and HCO₂Me-d_3 gradually increased in intensity, indicating a complete decarbonylation of 7 in about two weeks.
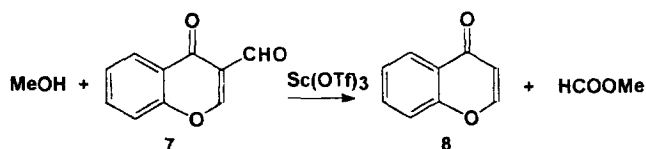
These and further results clearly indicated a strict correlation between the rate of $Sc^3(OTf)_3$ catalyzed decarbonylation reaction of aromatic aldehydes and the electron density on the aromatic ring, in accordance with the proposed mechanism (Scheme 1). For example, 2,4-dimethoxy and 2,6-dimethoxybenzaldehyde upon exposure to $Sc(OTf)_3$ (0.16 equiv.) were decarbonylated for about 10 % on heating for 1 h in MeOH solution, while 4-methoxybenzaldehyde did not react at all. Since the UV and NMR spectra of the above aldehydes clearly showed that corresponding acetals were formed as rapidly as those of **1** and **7**, these findings suggest that the reaction of formation and/or decomposition of the Wheland complex (see structure **6** in Scheme 1) are rate-controlling.

In order to better evaluate the catalytic activity of $Sc(OTf)_3$, we then explored the effects of other Lewis acid salts on the decarbonylation of 2,4,6-trimethoxybenzaldehyde (**1**). Thus, we examined scandium salts containing a counterion more coordinating than the triflate, and triflates of rare earth metals possessing a larger cation size than Sc^{3+}. Aldehyde **1** was not decarbonylated in MeOH solution at 25 °C with 1 equiv $ScCl_3$, while on exposure to 1 equiv $La(OTf)_3$ or $Y(OTf)_3$ **1** was completely decarbonylated in MeOH solution at reflux only after 20 h and 5 h, respectively.[22] The precisely tuned catalytic properties of $Sc(OTf)_3$ were further demonstrated by the inertness of **1** towards other metal triflates, like LiOTf, $Mg(OTf)_2$ or $Zn(OTf)_2$. On the other hand, the latter salts did not alter at all the UV spectra of **1** in MeCN, pointing out, once more, to a strict correlation between the highly accelerating effects of $Sc(OTf)_3$ on the decarbonylation of aromatic aldehydes and the strong coordinating power of the Sc^{3+} ion to the carbonyl group.

In conclusion, these results underline the unique features of $Sc(OTf)_3$ which catalyzes the decarbonylation of electron-rich aromatic aldehydes under much milder conditions than mineral acid solutions of relatively high strengths.[8] The reaction seems to follow a relatively new mechanism (Scheme 1). We anticipate that a mixture of $Sc(OTf)_3$ and a strong acid might exert in several instances catalytic effects comparable to the common superacidic systems.

Experimental

Aromatic aldehydes are commercially available (Aldrich or Acros). MeCN and MeOH are reagent grade solvents. $Sc(OTf)_3$ was freshly prepared from Sc_2O_3 and TfOH and dried at 100 ° C over P_2O_5 in an Abderhalden drying apparatus.[2c] UV spectra were recorded in the 200 - 400 nm range with a HP 8452A diode array spectrophotometer. NMR spectra were recorded on a Bruker ACE 300 (300 MHz) spectrometer in MeCN-d_3 or MeOH-d_4 with TMS as an internal standard. Chemical shifts are given in ppm (δ scale).

Typical experimental procedure for the decarbonylation of aromatic aldehydes: The required amount of $Sc(OTf)_3$ (see text) was added to 2,4,6-trimethoxybenzaldehyde (0.33 mmol) in MeOH solution (2.5 mL) and the reaction flask, equipped with a short Dufton column and a $CaCl_2$ tube, was kept in a thermostatic bath at the desired temperature. The reaction was monitored by TLC until disappearance of the starting substrate. After cooling the stirred mixture to room temperature H_2O was added and the product

directly filtered off. 1,3,5-Trimethoxybenzene, identified by its m.p. (51-53 ° C) and ^{1}H NMR spectrum, was obtained in 90 % isolated yield.

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9. At higher concentrations of aldehyde 1 and Sc(OTf)3 we observed the formation of condensation by-products which will be reported in a forthcoming paper.

10. The concomitant decomposition of 1 was very slow at the concentration (ca. 10^{-5} M) suitable for the spectrophotometric studies and did not affect measurements significantly.

11. Δ δ values (ppm) observed on addition of Sc(OTf)3 (2 equiv.) to 1 in MeCN-$d3$; (^{1}H): 0.00 for H-3, -0.69 for H-5, +0.11 and +0.08 for 4-OMe and 2-OMe, respectively; (^{13}C): -2.60 for C-1, +4.43 for C-2, +0.79 for C-3, +7.82 for C-4, +3.93 for C-5, +1.25 for C-6, +1.07 for C-7.

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14. Discrepancies in the experimental values obtained from different determinations are to be ascribed to the unavoidable presence of H_2O , which causes dissociation of complex **2**. Indeed, as little as 0.5% H_2O caused the UV spectrum of **2** to become that of uncomplexed aldehyde **1**.

15. The catalyst is indicated as Sc^{3+} in eq 4 since the Job[12] and Hildebrand[13] methods gave good results by employing the total Sc^{3+} concentration. On the other hand, dissociation of rare earth triflates [RE(OTf)3] in MeCN solution strongly depends on the amount of H_2O (Di Bernardo, P.; Cioppin, G.R.; Portanova, R.; Zanonato, P.L. *Inorg.Chim.Acta* **1993**, *207*, 85).

16. The same ultraviolet changes were observed on adding MeOH to **1** and Sc(OTf)3 in MeCN solution.

17. CN of Sc^{3+} can reach 9 (Bisi Castellani, C.; Carugo, O.; Giusti, M.; Sardone, N. *Eur. J .Solid State Inorg.Chem.* **1995**,*32*, 1089).

18. The carbonyl group in the bulky complex **3** is likely activated not only by complexation with Sc^{3+} but also by the lack of coplanarity with the aromatic ring due to steric hindrance with the *o*-methoxyl groups.

19. The catalytic activity of lanthanide (III) ions in acetal formation is well documented; see: (a) Luche, J.L.; Gemal, A.L. *J.Chem.Soc.Chem.Commun.* **1978**, 976. (b) reference 2a.

20. This proton should be at least as acid as Me*OH* in the presence of Sc(OTf)3.

21. Decarbonylation of **1** via the aldehyde hydrate ArCH(OH)2 was considered an unlikely path in mineral acid media [8].

22. In accord with the reduced catalytic activity relative to Sc(OTf)3 , Y^{3+} and La^{3+} triflates caused a much less pronounced red shift for the [1]La band in the UV spectra of **1** in MeCN solution.