Formyl Onium Salts: Synthesis and Decomposition Pathways

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Isolable formyl-pyridinium and -imidazolium salts are generated by treating Lewis acid–base pairs of type Me_3SiA–N-heterocycle (A = leaving group) with acetic formic anhydride; their thermal and base-catalysed decarbonylation is discussed in the light of theoretical data.

The stability of formyl derivatives HCO–X depends critically upon the leaving group properties of X and decreases accordingly along the series X = NR_2, OR, O(CO)R, halogen. This becomes particularly evident for the subgroup of formylhalides in which only the fluoride represents a thermally stable compound, with the heavier homologues becoming increasingly unstable towards dissociation into HX and CO.[1,2] Not surprisingly systems with positively charged leaving groups have never been described. We now report the first synthesis of stable salts of type $(HCO–X)^+A^-$, in which X represents an onio ligand, and some of their characteristic properties.

Recently we have demonstrated[3,4] that stable Lewis acid–base pairs of type Me_3SiA–4-dimethylaminopyridine (DMAP) (A = leaving group) are sufficiently nucleophilic at the ring nitrogen to allow transamination reactions with electrophilic halogen and polyhalogen compounds RX according to equation (1). In view of the high oxygenophilicity of silicon it seemed attractive to react reagents of type (1) with electrophilic oxygen compounds. With acetic formic anhydride a clean reaction according to equation (2) was observed. Salts (2a,b) precipitate directly in pure form from the reaction mixture, while in the case of the more soluble salt (2c) this can be achieved by addition of CCl_4. Average yields are between 70—90%. Salts (2) have been fully characterized.† They

represent the first N-formylpyridinium salts and, beyond that, the first formyl-onium salts. An i.r. band at ca. 1750 cm^{-1} and an ¹H n.m.r. signal at ca. δ 9.52 (s) are highly diagnostic of this class of compounds. Salts (2) are colourless, highly hygroscopic substances of surprising thermal stability. When heated in bulk above 110 °C they decarbonylate quantitatively according to equation (3). The counter anion has little, if any, effect on the decomposition range, which points to a unimolecular α-elimination within the cationic moiety. However, catalytic amounts of free DMAP cause effective decarbonylation of salts (2) within minutes at −20 °C and above. This observation demonstrates (i) that decarbonylation of (2) can be conducted according to a (base-catalysed) E2-type elimina-

$$[Me_3SiA/DMAP] + R-X \longrightarrow [R-DMAP]^+A^- + Me_3SiX \quad (1)$$

(2)

(3)
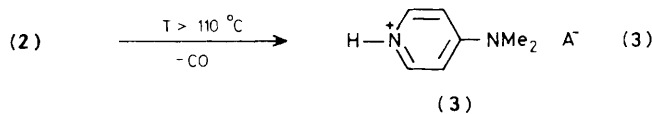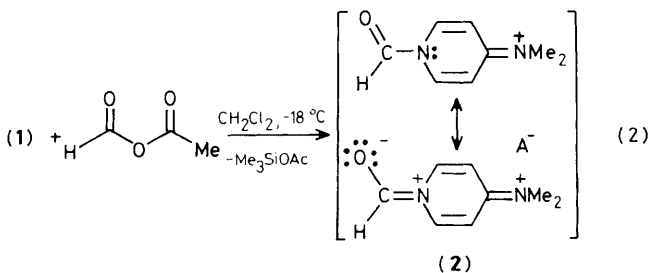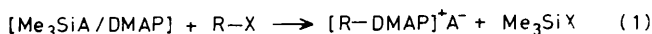
a; $A^- = Br^-$
b; $A^- = I^-$
c; $A^- = CF_3SO_3^-$

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† Salts (2a—c) yielded satisfactory C, H, N analyses. The spectroscopic data of the formyl-onium moities did not change with change of counter anion. Synthesis of (3a—c): to a solution of DMAP in dichloromethane an equimolar amount of Me_3SiA (A = Br, I, CF_3SO_3) is carefully added (exothermic reaction). After the homogeneous solution has cooled to room temperature, it is slowly added to acetic formic anhydride in dichloromethane cooled to −18 °C. The precipitate is filtered at ambient temperature, washed with dichloromethane and dried under vacuum to give (2a—c) in 80% yield; (2c) was washed with tetrachloromethane.

Selected spectroscopic data for (2a): i.r. (Nujol): 1750(s), 1635(vs), 1580(s) cm^{-1}; field desorption mass spectrum (100 °C, 4 kV): m/z = 151 (M^+ − Br), 123 (M^+ − Br −CO); ¹H n.m.r. (400 MHz, in $CDCl_3$–CD_3CN): δ 3.39 (s, 6 H), 7.89 (m, AA'BB', 4 H), 9.52 (s, br., 1 H); ¹³C n.m.r. ($CDCl_3$–CD_3CN): δ 42.01 (NMe_2), 108.72 (C-3, C-5); 137.07 (C-2, C-6); 159.85 (C-4); 161.55 (CHO).
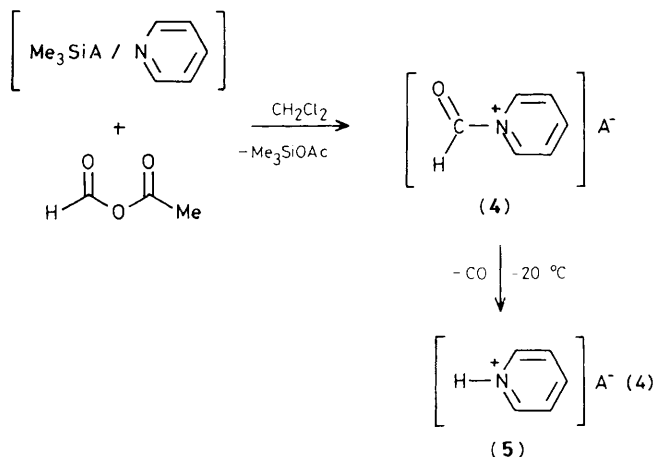
tion and (ii) that free DMAP is not present under the reaction conditions of equation (2).[5]

Attempts to replace DMAP by pyridine led to rapid decarbonylation according to equation (4) even at low temperature. What makes (4) so unstable with respect to α-elimination as compared to its DMAP counterpart (2)? One obvious explanation could be resonance stabilization of the type indicated in equation (2), which is structurally only possible for (2), but not for (4). This assumption, however, receives little support from MNDO model calculations.[6] Unimolecular decomposition according to (2) → (3) [case (a)] and (4) → (5) [case (b)] was calculated to be distinctly endothermic for both cases, although somewhat less so for the former process [$\Delta H_{decomp.}$: case (1): 61.9 kJ; case (b): 70.9 kJ]. Furthermore σ- and π-bond orders are of comparable size in both classes of formyl-onium systems; σ-bond order: 0.54 in (2) vs. 0.53 in (4); π-bond order: 0.25 in (2) vs. 0.21 in (4).

Viewed together these theoretical data do not satisfactorily account for the failure to synthesize (4). Kinetic factors are probably responsible for the complete decomposition of (4) under the reaction conditions of equation (4), the most likely being base-induced α-elimination by free pyridine. The presence of the latter can be safely assumed, as adduct formation between pyridine and trimethylsilylating agents is known to be incomplete in solution.[5]

In the synthetic procedure outlined above, DMAP can be successfully replaced by N-methylimidazole. Thus stable N-formylimidazolium salts were obtained in high yields.

Formyl-onium salts hold great promise as formyl transfer reagents.[7] Preliminary results confirm this expectation. Thus in qualitative tests p-thiocresol, N-methylaniline, and phenol were S-, N-, or O-formylated respectively by stirring with (3a) in CH_2Cl_2. Under Friedel–Crafts conditions anisole and N,N-dimethylaniline were ring formylated in moderate yields.

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