Metal-assisted Electrophilic Reactions on Carbon Dioxide: Synthesis of Mixed Carboxylato–Carbamato Anhydrides

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Mixed carboxylato–dialkylcarbamato anhydrides $R''C(O)O(O)CNR'_2$ were obtained at room temperature from the reaction of several *N,N*-dialkylcarbamato metal derivatives with an acyl halide, $R''COCl$.

Thermodynamically stable carbon dioxide is reactive towards nucleophilic reagents, as shown by the well established syntheses of carboxylic acids from Grignard reagents, the synthesis of salicylic acid from sodium phenoxide,[1] the formation of HCO_3^- in alkaline solution,[2] the synthesis of urea[3] and of the $R_2NCO_2^-$ anion from ammonia (R = H) or from secondary amines,[4] and the *C*-co-ordination of carbon dioxide to electron-rich transition metals.[5] In contrast *O*-co-ordination of CO_2 to transition or non-transition metal complexes or reactions of CO_2 with electrophiles are unprecedented in the literature.

We have now found that metal–dialkylcarbamato complexes[6] react with acyl halides to give mixed carboxylato–carbamato anhydrides. Reaction (1) can therefore be proposed as an alternative method of preparation of mixed anhydrides.[7] Since metal dialkylcarbamato complexes of transition metals can be prepared from a metal halide, secondary amine, and CO_2 at room temperature and atmospheric pressure, the combined reactions (2) and (3) represent a metal-assisted synthesis of mixed anhydrides from CO_2, R'_2NH, and $R''COCl$.

The new mixed anhydrides ($R' = Et, Pr^i$; $R'' = Me, Ph$), some of them ($R' = Et, Pr^i$; $R'' = Me$) unstable in solution at room temperature, were characterized spectroscopically in solution (νCO), analytically, and by spectral methods (mass and ^{13}C n.m.r.) in the case of the stable derivative with $R' = Pr^i$ and $R'' = Ph$.

$$2R'_2NH + CO_2 + R''COCl \xrightarrow{[M]} R'_2NC(O)O(O)CR'' + R'_2NH_2Cl \quad (1)$$

$$\frac{1}{n}MCl_n + CO_2 + 2R'_2NH \longrightarrow R_2NH_2Cl + \frac{1}{n}M(O_2CNR'_2) \quad (2)$$

$$\frac{1}{n}M(O_2CNR'_2) + R''COCl \longrightarrow R'_2NC(O)O(O)CR'' + \frac{1}{n}MCl_n \quad (3)$$

(n = oxidation state of the metal; M = Na, Cu^{II}, Ti^{III}, V^{III})

The observed attack of the electrophilic acyl halide at the metal-co-ordinated oxygen of the carbamato group is believed to arise from the mutual reduction of *N*-nucleophilicity and *C*-electrophilicity within the carbamato group itself. The reaction reported here is reminiscent of metal acetato complexes reacting with RCOCl to give the metal halide and the corresponding carboxylic anhydride,[8] but with the additional advantage in our case that the organic products contain a new nitrogen functionality.

Since the mixed anhydrides can be obtained from sodium dialkylcarbamate, see equation (1), and the dialkylcarbamate anion $R_2NCO_2^-$ can exist in solutions containing R_2NH and carbon dioxide,[9] the present data may be helpful in analysing by a common mechanism the earlier results concerning the preparation of urethanes from carbon dioxide, secondary amines, and alkyl halides with[10a] or without[10b] metal assistance.

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