

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, $R''COCl$.

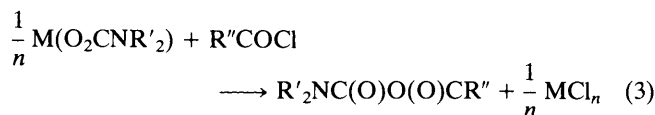
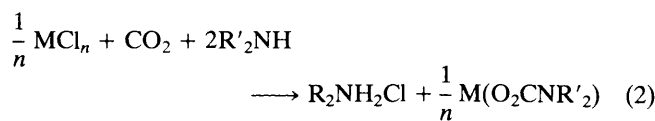
Thermodynamically stable carbon dioxide is reactive towards nucleophilic reagents, as shown by the well established syntheses of carboxylic acids from Grignard reagents, the synthesis of salicylic acid from sodium phenoxide,¹ the formation of HCO_3^- in alkaline solution,² the synthesis of urea³ and 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 com-

plexes⁶ 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 CO₂ at room temperature and atmospheric pressure, the combined reactions (2) and (3) represent a metal-assisted synthesis of mixed anhydrides from CO₂, R'₂NH, and R''COCl.

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



(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 R₂NCO₂⁻ can exist in solutions containing R₂NH 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.

This work was supported by Consiglio Nazionale delle Ricerche (C.N.R., Roma) through Progetto Finalizzato di Chimica Fine e Secondaria. Thanks are due to Dr. A. Morvillo for the mass spectral data and to Dr. A. Segre for measuring the ¹³C n.m.r. spectrum of Pr₂NC(O)O(O)CPh.

Received, 24th March 1986; Com. 397

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