Reaction of Lead Tetra-acetate with Primary Amides. Formation of Acylamines

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TREATMENT of primary carboxamides with iodine–lead tetra-acetate affords *N*-iodo-amides, photolysis of which provides a route to lactones when compounds suitably constituted for intramolecular hydrogen-atom transfer are employed.[1]

We have now observed that reaction of a primary amide (I) in benzene or benzene–acetic acid with lead tetra-acetate alone follows a completely different course and yields a mixture of the appropriate acylamine (II) and dialkylurea (III). Thus pentanamide when heated under reflux for 4 hours with 1 molar equivalent of lead tetra-acetate in benzene gave *N*-butylacetamide (45%) and *NN'*-dibutylurea (5%). When neat acetic acid is used as solvent the formation of dialkylurea appears to be suppressed. The yields of products obtained from various amides are shown in the accompanying Table.

Amide (I)		Yields (%)	
R	Solvent	Acylamine (II)	Dialkylurea (III)
Bu^n	Benzene	45	5
Pentyl	"	40	5
Cyclohexyl	Benzene–acetic acid	65	8
"	Acetic acid	64	nil
Heptadecyl	Benzene–acetic acid	61	9
Benzyl	Acetic acid	67	nil
Dec-9-enyl	Benzene–acetic acid	53	3
24-Nor-5β-cholanyl	" " "	81	nil

Because it proceeds under mild conditions the reaction may be useful for synthesis or degradation of compounds containing reactive groups. The successful preparation of *N*-dec-9-enylacetamide provides a case in point. However, the reaction fails with benzamide, presumably because of

$$\underset{\text{(I)}}{RCO{\cdot}NH_2} + Pb(OAc)_4 \longrightarrow RCO\dot{N}{\cdot} + Pb(OAc)_2 + HOAc$$

$$\begin{tikzcd}
RCO\dot{N}{\cdot} \arrow[r] & RNCO \arrow[r, "HOAc"] & RNH{\cdot}COOAc \arrow[r] \arrow[dr] & RNHAc \quad \text{(II)} \\
 & & & \underset{\text{(III)}}{RNH{\cdot}CO{\cdot}NHR}
\end{tikzcd}$$

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[1] D. H. R. Barton and A. L. J. Beckwith, *Proc. Chem. Soc.*, 1963, 335; D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.*, 1965, 181.

further attack of lead tetra-acetate on the primary product, acetanilide.

Having regard to the intermediate formation of alkyl isocyanate, detected spectroscopically, and to the general similarity between this reaction and the Curtius reaction when conducted in acetic acid,[2] we suggest that the mechanism involves formation and rearrangement of an acyl nitrene.

The scope and mechanism of the reaction are under investigation.

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[2] P. A. S. Smith, *Org. Reactions*, 1946, **3**, 337; R. G. Arnold, J. A. Nelson, and J. J. Verbanc, *Chem. Rev.*, 1957, **57**, 47.