The Reaction of Lead Tetra-acetate with Phenylmethylamines

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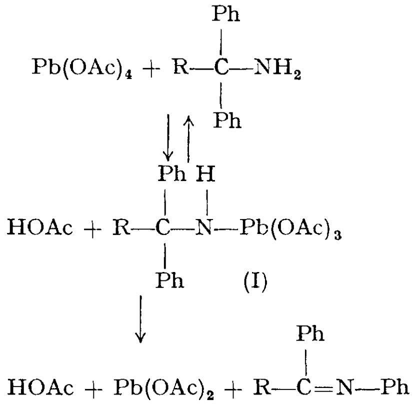
THE formation of amines by the Hofmann rearrangement of *N*-halogenoamides and, more recently, the isolation of isocyanates from the reaction of lead tetra-acetate with primary amides,[1] illustrate the similarity in the decompositions of *N*-lead- and *N*-halogeno-amide intermediates. Triarylmethyl-*N*-halogenoamines under basic conditions produce imino-compounds by aryl migration.[2] The reaction of lead tetra-acetate with arylmethylamines has not been reported, so I treated lead tetra-acetate with triphenylmethylamine[3] and 1,1-diphenylethylamine.[4]

Lead tetra-acetate (0·012 mole in 100 ml. of anhydrous benzene) was refluxed (4 hr., N_2) with triphenylmethylamine (0·01 mole). The mixture was filtered and the benzene solution was washed with ethylene glycol, water, aqueous sodium carbonate, and water and dried. The benzene was removed under vacuum. The residue (from ethanol) gave benzophenone anil (85%), m.p. 110—112° (lit.[5] 112—113°). The structure was confirmed by i.r. (C=N–, 1625 cm.$^{-1}$ (CCl_4)] and n.m.r. spectra [m, τ 2·2—3·5 (CCl_4)] and quantitative acid hydrolysis [to give aniline, identified as benzanilide, and benzophenone, m.p. and mixed m.p. 48—50° (2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 238—239°)]. The same reactants (50% excess of lead tetra-acetate) when refluxed for ½ hr. gave a 90% yield. The lead tetra-acetate must be freed of acetic acid under vacuum otherwise the major product is the acylated amine. When the above reaction was conducted in 75% cyclohexene–benzene (to trap a possible nitrene intermediate), no aziridine could be detected, only (II) (90%). With 1,1-diphenylethylamine[4] the acetophenone anil was isolated (70%), m.p. 42—43° (lit.[6] 41°). Upon acid hydrolysis it produced acetophenone, identified as its 2,4-dinitrophenylhydrazone, and aniline, identified as benzanilide.

An attractive rationale for the reaction is as follows:



$$Pb(OAc)_4 + R\text{—}\overset{\displaystyle Ph}{\underset{\displaystyle Ph}{C}}\text{—}NH_2 \rightleftharpoons HOAc + R\text{—}\overset{\displaystyle Ph}{\underset{\displaystyle Ph}{C}}\text{—}\overset{\displaystyle H}{N}\text{—}Pb(OAc)_3 \quad (I) \longrightarrow HOAc + Pb(OAc)_2 + R\text{—}\overset{\displaystyle Ph}{C}=N\text{—}Ph$$

(IIa) R = Ph
(IIb) R = Me

In this instance, the concerted ionic or free radical breakdown of (I) to (II) seems probable.

The almost quantitative conversion would provide a most reliable determination of phenyl as against *p*-substituted phenyl migration and thus should offer additional evidence for direct production of (II) from (I).

(*Received, June 24th,* 1968; *Com.* 840.)

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