Tetrahedron Letters No. 7, pp 499 - 502, 1973. Pergamon Press. Printed in Great Britain.

REACTION OF KETONITRONES WITH LEAD TETRAACETATE. CLEAVAGE OF THE C=N BOND

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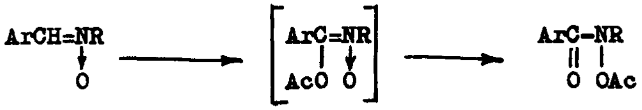
(Received in UK 6 December 1972; accepted for publication 8 January 1973)

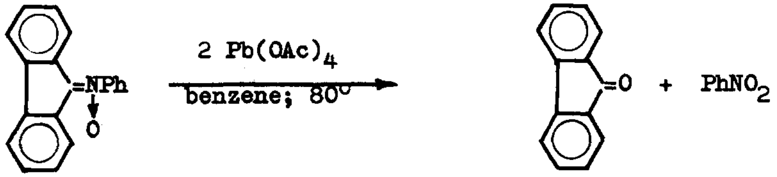
Earlier (1) we showed that the reaction of aromatic aldonitrones with lead tetraacetate is accompanied by rearrangement to give as final products N-aroyl-O-acetylhydroxylamines (III). Similar results were later also obtained by Gutteridge (2) with cyclic aldonitrones (pyrrolidine-N-oxides). Although, ketonitrones RR'C=N(O)R" are obviously incapable of such transformations, some of them, such as C,C,N-triphenylnitrone and C,C-diphenyl-N-benzylnitrone, in the presence of $Pb(OAc)_4$ in benzene solution form EPR detectable nitroxide radicals $Ph_2C(OAc)N(R)O^{\bullet}$ (IV) belonging to the same type as the nitroxides resulting from interaction of $Pb(OAc)_4$ with various aldonitrones (I) (3).



I II III

These facts induced us to carry out a chemical study of the reaction of ketonitrones with $Pb(OAc)_4$, as a result of which it was found that, contrary to aldonitrones, the ketonitrones under the experimental conditions are split at the C=N bond. The most characteristic examples are C,C,N-triphenylnitrone $Ph_2C=N(O)Ph$, N-fluorenylideneaniline-N-oxide (V) and C,C-diphenyl-N-benzylnitrone $Ph_2C=N(O)CH_2Ph$. On treating triphenylnitrone with 1 mole of $Pb(OAc)_4$ in abs. benzene (1 hr. at room temperature) the former is smoothly cleaved

to benzhydrylidenediacetate $Ph_2C(OAc)_2$ (yield ca. 90% according to GLC data) and nitrosobenzene.



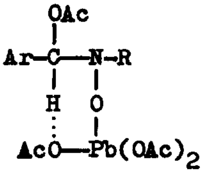
V

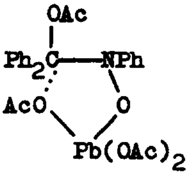
N-Fluorenilideneaniline-N-oxide (V) reacts with $Pb(OAc)_4$ only on heating. After refluxing for 2 hrs with 1 mole of $Pb(OAc)_4$ in benzene, this nitrone yielded fluorenone, nitrosobenzene and nitrobenzene, as well as a certain amount of the unreacted material. Evidently under these conditions part of the $Pb(OAc)_4$ is consumed in oxidizing nitrosobenzene. In fact, the only products of a similar reaction of nitrone (V) with 2 moles of $Pb(OAc)_4$ were fluorenone (ca. 80% yield) and nitrobenzene (ca. 100% yield). It was shown by special experiments that no intermediate formation of 9,9-diacetoxyfluorene takes place; this compound /obtained by treating fluorenone hydrazone with lead tetraacetate, cf. (4)/ was isolated unchanged after refluxing for two hrs with lead tetraacetate in benzene.

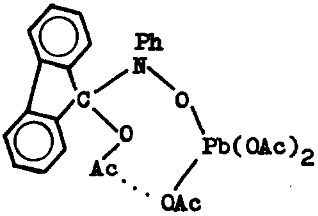
C,C-Diphenyl-N-benzylnitrone also reacts with $Pb(OAc)_4$ by cleavage of the C=N bond, but in this case, because of the presence of a benzyl CH_2 group, the reaction is more complicated; only a 25% yield of benzhydrylidenediacetate being obtained on reacting this nitrone with 2 moles of $Pb(OAc)_4$ (benzene, 100 hrs, room temperature).

Although, as in the case of aldonitrones, nitroxide radicals which could be regarded as products of the addition of the acetoxy radical AcO• to the ketonitrones were revealed with the aid of EPR spectroscopy when C,C,N-triphenylnitrone and C,C-diphenyl-N-benzylnitrone (but not N-fluorenylideneaniline-N-oxide) were reacted with $Pb(OAc)_4$ (3), such type (IV) radicals are not intermediates in the interaction of keto- and aldonitrones with lead tetraacetate. This was confirmed by kinetic measurements, especially detailed in the case of C,N-diphenylnitrone, which showed the absence of any correlation between the rate of disappearance of the nitroxide PhCH(OAc)N(Ph)O• and the rate of formation of the reaction product (III; Ar = R =Ph).

We believe it most probable that the first stage of the $Pb(OAc)_4$ reaction with nitrones is 1,3-addition to the latter with the formation of RR'C(OAc)-N(R")$OPb(OAc)_3$ type adducts whose subsequent conversions proceeding via cyclic activated complexes are governed by the nature of the R and R' substituents on the nitrone C atom.


VI


VII


VIII

Thus, in the case of aldonitrones, the six-membered cyclic complex (VI) breaks down into C-acetoxynitrone (II), AcOH and $Pb(OAc)_2$, whereas in the case of C,C,N-triphenylnitrone, the five-membered complexes (VII) undergo fission to PhNO, $Ph_2C(OAc)_2$ and $Pb(OAc)_2$. However, with N-fluorenylideneaniline-N-oxide (V) steric hindrances apparently permit formation of only the seven-membered complex (VIII) which subsequently breaks down to Ac_2O, fluorenone, PhNO and $Pb(OAc)_2$.

The nitroxide radicals observed in the reaction of the nitrones with $Pb(OAc)_4$ apparently derive from side reactions, possibly by addition to the nitrones of acetoxy radicals formed in dissociation of $Pb(OAc)_4$ or by partial dissociation of the 1,3-adducts.

Although recent years have witnessed study of the reaction of lead tetraacetate with different types of C=N-containing compounds (5), rupture of this bond has been observed only for diazo compounds (4, 6-8) and Schiff bases (9, 10). Compared with the latter, cleavage in the ketonitrones occurs much more readily and more completely and the high yields of the products make the above reaction of promise for synthesis of various aromatic nitroso compounds.

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