Oxidation of Nitroalkanes with Lead Tetra-acetate

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Summary Lead tetra-acetate oxidizes nitroalkanes to *gem*-acetoxy-nitro-compounds.

ATTACK on activated C–H bonds by lead tetra-acetate gives rise to acetoxy-compounds.[1] We report the oxidation of nitroalkanes with this reagent, to give *gem*-acetoxy-nitro-compounds.

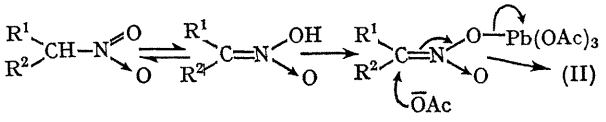
$$R^1R^2CH{\cdot}NO_2\ (I) \xrightarrow{Pb(OAc)_4} R^1R^2C(OAc){\cdot}NO_2$$

With nitromethane as solvent, oxidation of aldehydes with lead tetra-acetate gives acetoxynitromethane instead of the acetoxy-aldehyde. The reaction is a general one as shown by the similar oxidation of nitroethane and 2-nitropropane. The best results are obtained in nitroalkane as solvent, although benzene or dichloromethane may be used. In the latter solvent, the reaction is slower.

TABLE

(II) R^1	(II) R^2	B.p.	M_D^{20}	I.r. (CCl_4) $\nu_{C=O}$		ν_{NO_2}	N.m.r. (δ,CCl_4,Me_4Si)
H	H	67—68°/11 mm.	1·4135	1780	1580	1370	2·23(s,3H) 5·65(s,2H)
Me	H	71—72°/14 mm.	1·4095	1780	1570	1360	1·74(d,3H) 2·19(s,3H)
Me	Me	86—87°/18 mm.	1·4160	1775	1565	1350	6,11(q,1H) 1·86(s,6H) 2·11(s.3H)

Analysis of the products (v.p.c.) shows that *gem*-acetoxy-nitro-compounds (II) (see Table)† are the only products. We suggest the following mechanism for the reaction:



† Satisfactory analyses were obtained for all new compounds.

Compounds of structure (II; R^1 and R^2 alkyl groups) have been prepared thus:[3]

$$R^1R^2C{=}N{\cdot}OH \xrightarrow{Pb(OAc)_4} R^1R^2C(OAc){\cdot}NO \xrightarrow{H_2O_2} R^1R^2C(OAc){\cdot}NO_2$$

A radical mechanism is excluded since the reaction is unaffected by radical initiators; addition of a base (triethylamine) however, strongly accelerated the reaction.

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[1] R. Criegee in "Oxidation in Organic Chemistry," ed. K. B. Wiberg, Academic Press, New York, 1965, p. 305.
[2] J. J. Riehl and A. Fougerousse, *Bull. Soc. chim. France*, 1968, 4083.
[3] D. C. Iffland and G. X. Criner, *Chem. and Ind.*, 1956, 176.