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THE REACTION OF LEAD TETRAACETATE WITH HYDROCARBONS

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ABSTRACT: The free radical reaction of lead tetraacetate with hydrocarbons has been investigated. The products of these reactions are the acetate esters. The hydrogen abstracting species from lead tetraacetate is found to have a primary to secondary to tertiary selectivity of 1:27:123 based upon relative reactivities.

Crank, et al. (1) have reported an unusual free radical reaction of lead tetraacetate, LTA, with alkanes. In their report, hexane was converted into a mixture of 2-hexyl acetate and 3-hexyl acetate in about 50% yield based upon the LTA employed. None of the 1-hexyl acetate was reported. Even with very selectivity radicals, such as bromine atoms, or the radical from iodobenzene dichloride, some primary product is always detected (2). Due to our interest in the free radical functionalization of alkanes, we have reinvestigated the reaction of LTA with hydrocarbons and would like to report our preliminary results.

Cycloalkanes and alkanes react with LTA in acetic acid solutions to form the corresponding acetate esters (3). This reaction is slow, requiring from 10 days to 2 weeks for completion. The slowness of the conversion of LTA to products suggests that the reaction is proceeding via a very short chain process, or more likely that the conversion is not a chain reaction.

Several representative compounds are shown in Table 1 with their yield based upon the LTA consumed. In all cases the yields are in the neighborhood of 50%, in keeping with Crank's earlier report (1). Also, no detectable primary product from either 2,3-dimethylbutane or pentane was found by gas chromatographic analysis of the reaction mixtures. The lack of primary attack by the hydrogen abstracting radical is very unusual, and is reminiscent of earlier reports for the free radical photooximation of alkanes by nitrosyl chloride, where only secondary products were identified and none of the products expected from primary or tertiary attack were detected (4).

Table 1: Products and yields in the reaction of lead tetraacetate with selected hydrocarbons.

hydrocarbon	products (% yield)
cyclohexane	cyclohexyl acetate (46%), cyclohexanol (7%)
cycloheptane	cycloheptyl acetate (57%)
pentane	2-pentyl acetate (32%), 3-pentyl acetate (24%)
2,3-dimethylbutane	2,3-dimethyl-2-butyl acetate (53%)
adamantane	1-adamantyl acetate (33%), 2-adamantyl acetate (2.5%)

To obtain a better understanding of the reaction intermediates, several hydrocarbons of different structures were competitively allowed to react with LTA and the results are presented in Table 2 (5). The method of relative reactivities, in which a limited amount of LTA competes for 2 substrates has the advantage, especially in this case, that since the disappearance of the substrate is being measured, the fate of the intermediates or products is of no consequence. The non-zero relative rate of reaction obtained for 2,2,3,3-tetramethylbutane shows that primary hydrogens are not inert to this reagent, and that the lack of detectable primary product must arise through secondary reactions of the initially formed materials. Using the reactivities of cyclopentane, 2,3-dimethylbutane, and 2,2,3,3-tetramethylbutane from Table 2, an approximate primary to secondary to tertiary selectivity can be calculated

Table 2: The relative reactivities of several hydrocarbons to the reactive intermediate from LTA.

hydrocarbon	relative reactivity
cyclohexane	1.00*
cyclooctane	3.86±0.28
cyclopentane	2.55±0.28
2,3-dimethylbutane	2.43±0.18
2,2,3,3-tetramethylbutane	0.17±0.04

*assigned a value of 1.00

for the reactive intermediate from LTA as 1:27:123.

Previously, Heiba (7) and Walling (8) have suggested that the methyl radical is the hydrogen abstracting species in the reactions of LTA with aromatic hydrocarbons, Scheme 1:

Scheme 1:

$$\begin{array}{llr}
\text{LTA} \longrightarrow \text{Pb(OAc)}_3 + \text{CH}_3\text{CO}_2\cdot & & \text{(rxn 1)} \\
\text{CH}_3\text{CO}_2\cdot \longrightarrow \text{CO}_2 + \text{CH}_3\cdot & & \text{(rxn 2)} \\
\text{RH} + \text{CH}_3\cdot \longrightarrow \text{R}\cdot + \text{CH}_4 & & \text{(rxn 3)} \\
\text{R}\cdot + \text{LTA} \longrightarrow \text{Pb(OAc)}_3 + \text{ROAc} & & \text{(rxn 4)} \\
\text{Pb(OAc)}_3 \longrightarrow \text{Pb(OAc)}_2 + \text{CH}_3\text{CO}_2\cdot & & \text{(rxn 5)}
\end{array}$$

This pathway however does not seem to be operative in the reactions with alkanes and cycloalkanes, since Pryor (9) has reported the selectivity of the methyl radical to be 1:7:50. The exact nature of the hydrogen abstracting species and the mechanistic pathway for the reaction of LTA with aliphatic hydrocarbons is currently under investigation (10).

References and Notes:

1. R.D. Bestre, E.R. Cole, and G. Crank, *Tetrahedron Letters*, **24**, 3891 (1983).
2. D.D. Tanner and G. Gidley, *J. Am. Chem. Soc.*, **89** 673 (1967).
3. experimental procedure: To a Pyrex ampoule was added 2mL of a 0.22M LTA in acetic acid solution, and 0.5mL of the hydrocarbon. The tube was degassed by the freeze-thaw-pumping method, sealed and wrapped in foil. The tube was placed in a water bath at 80°C for from 10 days to 2 weeks. The tube removed, opened, and an inert internal standard added. The reaction mixture was tested for completion of reaction with either water or potassium iodide solution. The contents of the tube were analyzed by GC on either a 6' x 1/4" 10% SE-30 or a 6' x 1/4" Ucon oil 200 glpc column. Products were identified by GC retention times and spiking using both columns. Yields are based upon the amount of the LTA present and calculated from the molar amount of the added standard.
4. M. W. Mosher and N.J. Bunce, *Can. J. Chem.*, **49**, 28 (1971) and references therein.
5. competition experiments were carried out in acetic acid solution in sealed, degassed ampoules as previously reported by this laboratory (6).
6. J.M. Krasniewski, Jr., and M.W. Mosher, *J. Org. Chem.*, **39**, 1303 (1974).

7. E.I. Heiba, R.M. Dessau, and W.J. Koehl, Jr., *J. Am. Chem. Soc.*, **90**, 1082 (1968).

8. C. Walling and J. Kjellgren, *J. Org. Chem.*, **34**, 1489 (1969).

9. W.A. Pyror, U. Tonellato, D.L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969).

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