235. *Selective Oxidations with Red Lead.*

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Red lead, in presence of acetic acid, can be used in many cases for the selective oxidation of glycols, α-hydroxy-acids, and certain amino-compounds in place of lead tetra-acetate or periodic acid. The procedure is demonstrated by several examples.

Red lead (Pb_3O_4) has been already employed in isolated cases for oxidation, *e.g.*, for introduction of acetoxy-groups into alicyclic and semialicyclic hydrocarbons (Fieser and Cason, *J. Amer. Chem. Soc.*, 1940, **62**, 432); however, oxidation of α-glycols and related compounds with this directly applicable, comparatively inexpensive oxidant appears not to have been systematically investigated. Oxidation with red lead is essentially oxidation with lead tetra-acetate under modified conditions (Vargha, *Nature*, 1948, **162**, 927) and in most of the cases the results are the same with both methods. In the present paper we report the behaviour of polyhydric alcohols, hexoses, hexosides, and some other substances in the presence of red lead in 25% acetic acid.

In dilute acetic acid the reduction and hydrolysis of transiently-formed lead tetra-acetate are competing with each other. Diethylidene sorbitol, pinacol, and phenyl-D-glucosotriazole, although consuming the oxidant in but 8—9 hours at room temperature, appeared to suppress hydrolysis completely, while with ethylene glycol, α-methylglucoside, or alanine considerable hydrolysis within a few minutes was observed. Oxidation of polyhydric alcohols and of α-hydroxy-acids proceeds as with lead tetra-acetate in glacial acetic acid; differences are observed only with free hexoses, D-glucose and D-galactose, which react with red lead under influence of the water present not as ring but as open-chain compounds, *i.e.*, as in periodic acid oxidations. Ethylenediamine and alanine remain unchanged under the conditions employed, the oxidant suffering quantitative hydrolysis, but fission of (—)-ephedrine to benzaldehyde and acetaldehyde occurred quantitatively.

Red lead oxidation is particularly successful in the simple preparation of ethyl glyoxylate from ethyl tartrate (yield, 54%), as compared with the similar oxidation with lead tetra-acetate; in the latter case the semiacetal of ethyl glyoxylate is obtained in a yield not exceeding 40—45% and the process of isolation is rather lengthy (Criegee, Kraft, and Rank, *Annalen*, 1933, **507**, 159).

Satisfactory yields have been obtained also in the preparation of 4-formyl-2-phenyltriazole from phenyl-D-glucosotriazole (Hann and Hudson, *J. Amer. Chem. Soc.*, 1944, **66**, 735, obtained this product by periodic acid oxidation) and of L-xylose from 1 : 3-2 : 4-diethylidene sorbitol (cf. Appel, *J.*, 1935, 425; Hockett and Schäffer, *J. Amer. Chem. Soc.*, 1947, **69**, 849); in the latter case the oxidation product is converted by subsequent hydrolysis into the free sugar. These examples show that even substances practically insoluble in water or sensitive towards acids can be oxidized in dilute acetic acid solution with red lead.

EXPERIMENTAL.

Experiments were carried out with technical red lead (active oxygen content being assayed by titration with N-potassium permanganate) at room temperature in 25% acetic acid (purified by distillation from powdered potassium permanganate), 1 mole of Pb_3O_4 per 8·8 moles of acetic acid being employed. Mechanically-shaken, open vessels were used. The course of the reaction was followed by means of the decoloration of the mixture and by analysis of the end products.

For determination of the volatile end-products formaldehyde, acetaldehyde, and formic acid, lead was precipitated from the mixture by sulphuric acid and the filtrate was subsequently distilled. The distillate was then titrated iodometrically to determine the aldehyde content, while titration with permanganate gave the content of aldehyde plus formic acid. Carbon dioxide was determined volumetrically. Lead dioxide was separated from the mixture by centrifugation and washed with 5% acetic acid, dried, and weighed. The rate of oxidation depends on the nature of the substance to be oxidized and on the rate of conversion of the red lead into lead tetra-acetate, *i.e.*, on the temperature and on the concentration and quantity of the acetic acid solution. The rate of oxidation increases rapidly with the initial acetic acid concentration up to 25%, but thereafter does not change significantly. Red lead itself, in absence of acetic acid, does not bring about oxidation, whereas lead dioxide in dilute acetic acid shows an unspecific oxidative effect, the rate of which, however, may be neglected in comparison with that of the tetra-acetate.

Ethyl Glyoxylate.—To a solution of ethyl tartrate (20·6 g.; 0·1 mol.) in 25% acetic acid (200 c.c.) red lead (68·6 g., 0·1 mol.) was added in small portions during *ca.* 1 hour at 15—20°, with mechanical stirring. Stirring was continued until complete decoloration (8 hours) had occurred. The clear solution was then continuously extracted with ether for 7 hours, the ethereal solution being subsequently dried and evaporated. The remaining oil gave ethyl glyoxylate, b. p. 58—62°/14 mm. (11 g., 54%).

4-*Formyl-2-phenyltriazole.*—A suspension of phenyl-D-glucosotriazole (1·3 g., 0·005 mol.) in 25% acetic acid (40 c.c.) was stirred at 15—20° for 8 hours, red lead (13·72 g., 0·02 mol.) being gradually added during the first hour. The resulting mixture was filtered, and the solid extracted with boiling alcohol (15 c.c.). The aldehyde crystallized from the alcoholic extract after addition of 30 c.c. of water and had m. p. 68° (0·72 g., 83%).

L-*Xylose.*—To a solution of 1 : 3-2 : 4-diethylidene sorbitol (5·85 g., 0·025 mol.) in 25% acetic acid (50 c.c.) red lead (17·5 g., 0·025 mol.) was added within 30 minutes, at 15—20° with mechanical stirring. Stirring was continued until the red lead disappeared (10 hours). Then the lead was precipitated with 50% sulphuric acid at 0° and more sulphuric acid was added until the solution became approx. 0·2N. The mixture was warmed in an open flask on the water-bath until acetaldehyde had evaporated (about 5 hours) and was then exactly neutralized with barium hydroxide. The solid was removed and washed on the centrifuge, and the solution evaporated at 14 mm. The residue was freed from water by being distilled with alcohol and then crystallized from alcohol, yielding L-xylose (2 g., 50%), m. p. 146—147°.

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