[Contribution from the Chemical Laboratory of Northwestern University]

# THE ACTION OF LEAD TETRAACETATE ON DIHYDROPYRAN

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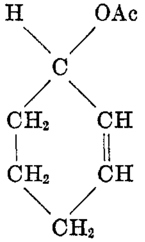
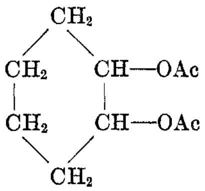
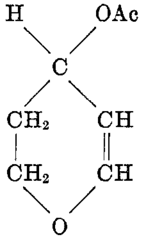
Criegee (1) found that 2-cyclohexenyl acetate (I), 1,2-cyclohexylene diacetate (II), and 1,2,3-cyclohexanetriol triacetate were formed by reaction of lead tetraacetate and cyclohexene. By analogy, lead tetraacetate should react with dihydropyran (5,6-dihydro-4*H*-pyran) to form 5,6-dihydro-4*H*-pyran-4-yl acetate (III), tetrahydropyran-2,3-diol diacetate, and tetrahydropyran-2,3,4-triol triacetate. If tetrahydropyran-2,3-diol could be prepared satisfactorily by this method it would furnish a second synthesis of the substance from dihydropyran, the first being from dihydropyran and hydrogen peroxide (2). As will be seen, however, no tetrahydropyran-2,3-diol diacetate was found. The actual products were the ester III, the acylal IV, tetrahydrofurfurylidene acetate, and materials that were non-volatile at 185° under 1 mm. pressure.



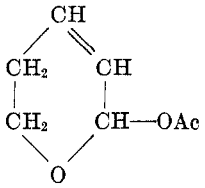
I



II



III



IV

III and IV appeared in a low-boiling cut. The presence of III in the mixture was demonstrated by the formation of formic acid on ozonolysis. The presence of IV was demonstrated by the fact that it underwent rapid hydrolysis at 25° either by dilute acid or by aqueous bicarbonate to a compound which gave the *p*-nitrophenylhydrazone of 5-hydroxy-2-pentenal rapidly under mild conditions. It is known that dihydropyran is only very slowly hydrolyzed by dilute acid at room temperature (3), hence the dihydropyran ring of III could not have opened under the mild hydrolytic conditions employed. Therefore, the *p*-nitrophenylhydrazone must have arisen from IV, not from III.

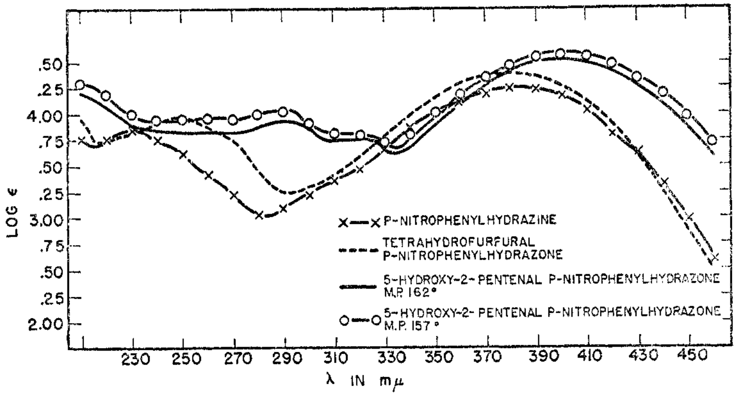


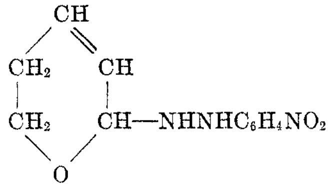
FIG. 1. U. V. ABSORPTION SPECTRA OF NITROPHENYLHYDRAZINES

Actually, not one but two isomeric *p*-nitrophenylhydrazones were obtained depending on whether the hydrolysate was treated with *p*-nitrophenylhydrazine in acid, or in basic or neutral solution. The one prepared in neutral solution could be changed into the other by warming with dilute acid.

The fact that the ultraviolet absorption spectra (Fig. 1) in 95% alcohol of these two nitrophenylhydrazones were practically identical supports the belief that both compounds possess comparable structures. Both are undoubtedly

$HOCH_2CH_2CH{=}CH{-}CH{=}NNHC_6H_4NO_2$

V



VI

5-hydroxy-2-pentenal *p*-nitrophenylhydrazones (V). If one of the hydrazones was of acyclic structure and the other of cyclic structure as N-(5,6-dihydro-2*H*-pyran-2-yl)-N′-*p*-nitrophenylhydrazine (VI), similar to glucosylphenylhydrazine (4), then quite different absorption spectra would have been anticipated.

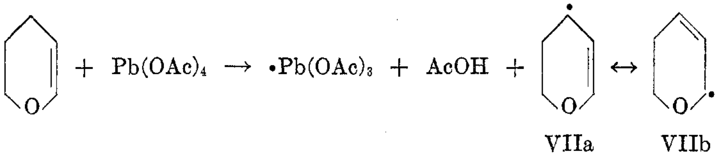
The position of the ethylenic double bond in V follows logically by its derivation from IV but direct support for the conjugate unsaturation is obtained by comparing the shift in the maxima of ultraviolet absorption for *p*-nitrophenylhydrazine at 384 mμ (log ε 4.24) and for an aldehyde derivative lacking conjugate unsaturation, namely, tetrahydrofurfural *p*-nitrophenylhydrazone at 381 mμ (log ε 4.37) with the maxima for the 162°- and 157°-derivatives at 399, 400 mμ (log ε 4.52, 4.56), respectively (Fig. 1). Bohlmann (5) has shown that this shift in *p*-nitrophenylhydrazones is characteristic of aldehydes containing conjugate unsaturation: crotonaldehyde *p*-nitrophenylhydrazone, 400 mμ (log ε 4.48); 2,4-hexadienal *p*-nitrophenylhydrazone, 414 mμ (log ε 4.64).

It is suggested that the 162°- and 157°-derivatives are *syn-anti* isomers at the C=N rather than *cis-trans* isomers at the C=C since the difference in the formation of the isomers is merely the *p*H of the medium in which they were prepared at room temperature. It is known, for example, that certain cyclic ketones give rise to *syn* or *anti* oximes (6) depending on the *p*H of the medium. Similarly, the formation of *syn* or *anti* forms of the 2,4-dinitrophenylhydrazones (7) of 1,2,3,4,4a,9,10,10a-octahydro-4-phenanthrenone depends on the amount of acid in the 2,4-dinitrophenylhydrazine solution employed.

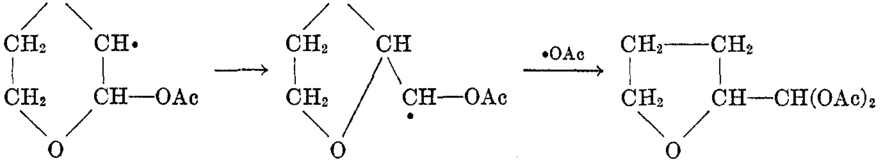
Tetrahydrofurfurylidene acetate (23% yield) was found in the high-boiling cuts. Its identity was established by its molecular weight, acetyl content, and its ready hydrolysis to tetrahydrofurfural. The latter was characterized as its dinitrophenylhydrazone, m.p. 134°, which did not depress the m.p. of an authentic sample (2b).

The work of Kharasch, Friedlander, and Urry (8) on reactions with lead tetraacetate, such as that with acetic acid at 120°, provides a basis for explaining the present results. These investigators speak against predissociation of lead tetraacetate into radicals and assume an initial bimolecular decomposition of lead tetraacetate with a hydrogen donor to yield radicals: $Pb(OAc)_4 + CH_3COOH \rightarrow \cdot Pb(OAc)_3 + \cdot CH_2COOH + AcOH$. A sequence of reactions was proposed to care for the fate of these two radicals.

The present reaction with dihydropyran proceeds at a lower temperature than Kharasch's with acetic acid, which is reasonable in view of the presence of allylic hydrogens in the dihydropyran thereby making the latter a better hydrogen donor. Following Kharasch, we assume the initial process to be this:



Such of the lead triacetate radical as does not disproportionate into lead di- and tetra-acetates may decompose into lead diacetate and the acetoxy radical. Then the latter may unite with the resonance hybrid (VIIa, VIIb) making up the dihydropyranyl radical to give III and IV. To a less extent, acetoxy appears to add to the double bond of dihydropyran to yield the new radical VIII. The production of tetrahydrofurfurylidene acetate is explained by assuming rearrangement of VIII and capture of a second acetoxy radical:



VIII

EXPERIMENTAL

*Lead tetraacetate and dihydropyran.* To a solution of 55 g. (0.66 mole) of dihydropyran in 150 ml. of dry, thiophene-free benzene was added 265 g. (0.6 mole) of lead tetraacetate in 1-g. portions. The mixture was shaken vigorously between additions. Heat was evolved and occasional cooling was necessary to keep the temperature below 30°. During this period of addition three crops of lead acetate were removed by filtration, and benzene washings of the solid were combined with the main solution, the final volume being 350 ml. When a slight excess of lead tetraacetate persisted for five minutes the addition was stopped.

The benzene was removed and the residue was separated by distillation under 8 mm. pressure into acetic acid, a low-boiling acetate containing acetic acid, and a liquid residue. Two fractional distillations at diminished pressure through a 15-cm. Vigreux column yielded these fractions:

A. 8 g. (20%) of acetic acid.

B. 29 g. (31%) of dihydropyranyl acetate, of which 17 g. (cut $B_1$) distilled at 69–71° (9 mm.), $n_D^{28}$ 1.4532, and 12 g. (cut $B_2$) was collected at 72–73°, $n_D^{28}$ 1.4542.

C. 10 g. of an intermediate fraction. On redistillation, in addition to fractions B and D there was obtained 3 g., b.p. 78–83 (3 mm.), $n_D^{27}$ 1.4577. This was saturated. Its mol. wt. was approximately 130. It had no effect on hot Benedict's reagent unless previously warmed with dil. hydrochloric acid. When treated at 0° with a trace of sodium methoxide in methanol, it gave a product from which no pure 2,4-dinitrophenylhydrazone was obtained.

D. 31 g. (23%) of tetrahydro-2-furfurylidene acetate, of which 25 g. was collected at 94–97° (2 mm.), $n_D^{27}$ 1.4414.

E. 7 g. of dark colored, viscous, ether-soluble oily residue.

*Characterization of D.* Scheibler, Satscheck, and Friese (9) described tetrahydrofurfurylidene acetate as boiling at 133° (29 mm.), $n_D^{20.3}$ 1.4405. Our fraction D was a colorless, water-insoluble, mobile liquid, inert to bromine in chloroform. It hydrolyzed rapidly when shaken with 1 *N* sulfuric acid at 90° into an aldehyde (Schiff test, and instantaneous reduction of neutral permanganate). The product was moderately soluble in water but could be readily extracted with ether. Its odor resembled acetaldehyde. When treated at room temperature with 2,4-dinitrophenylhydrazine hydrochloride in methanol the aldehyde gave tetrahydrofurfural 2,4-dinitrophenylhydrazone, m.p. and mixture m.p. 134° (2b). This derivative depressed the m.p. of 2,5-dihydroxypentanal 2,4-dinitrophenylhydrazone to 115–120°. When the acetate (2 g.) was deacetylated with a trace of sodium in methanol at 0°, the product also yielded the same dinitrophenylhydrazone (1.1 g., 62% yield).

*Anal.* Calc'd for $C_9H_{14}O_5$: Mol. wt., 202; Acetyl, 42.6.
Found: Mol. wt., 194; Acetyl, 41.0, 39.6.

*Characterization of B.*

*Anal.* Calc'd for $C_7H_{10}O_3$: C, 59.12; H, 7.09; mol. wt., 142.
Found: C, 58.89; H, 7.34; mol. wt., 141, 142.

*Reaction with bromine.* When titrated with bromine in chloroform at −78° the compound added 0.68, and 0.73 mole of bromine (separate runs). The adduct was sensitive to heat, turning dark quickly. It contained very active halogen, reacting with dry methanol or methanol containing pyridine with elimination of hydrogen bromide. The product still contained halogen as shown by sodium fusion. This could be removed in part by reaction with sodium methoxide in methanol at 20°, sodium bromide being precipitated. The product, however, still contained some halogen. No crystalline hydrazones could be prepared from it in acid solution.

*Acid hydrolysis to 5-hydroxy-2-pentenal.* Cut $B_1$ (0.6-g. portion) was shaken with 5 ml. of water containing a drop of conc'd hydrochloric acid. The acetate dissolved in less than a minute. A hot solution of 0.7 g. of *p*-nitrophenylhydrazine in methanol was added. The resulting crude derivative (1.27 g.) was crystallized from methanol, giving approximately 0.75 g., m.p. 155°. The theoretical yield would be 1.0 g.

*157°-p-Nitrophenylhydrazone.* After five recrystallizations of the above from methanol the substance appeared as leaf-shaped prisms of a brownish-orange color. It melted at 155.5–157° when immersed in a bath previously heated to 140°. The product from a similar hydrolysis of 1.03 g. of the total B cut gave 1.05 g. (62%) of crude *p*-nitrophenylhydrazone of 5-hydroxy-2-pentenal.

*Anal.* Calc'd for $C_{11}H_{13}N_3O_3$: C, 56.1; H, 5.53; N, 17.85.
Found: C, 56.25; H, 5.49; N, 17.82.

*2,4-Dinitrophenylhydrazone.* The product of a similar acid hydrolysis gave a 2,4-dinitrophenylhydrazone which separated as beautiful orange flat needles from methanol, m.p. 162.5–163.5° when immersed at 140°. 5-Hydroxy-2-pentenal 2,4-dinitrophenylhydrazone has been described as melting at 159–160° (10).

*Anal.* Calc'd for $C_{11}H_{12}N_4O_5$: C, 47.14; H, 4.32; N, 20.0.
Found: C, 47.06; H, 4.25; N, 19.90.

*Bicarbonate hydrolysis to 5-hydroxy-2-pentenal.* A 1.3-g. sample of the total low-boiling acetate (cut B) was shaken with a solution of 0.9 g. of sodium bicarbonate in 2 ml. of water and 1 ml. of methanol. There was a steady evolution of carbon dioxide, the hydrolysis being complete in half an hour. Six drops of acetic acid were added, giving a solution faintly alkaline to litmus.

*162°-p-Nitrophenylhydrazone.* A hot saturated methanol solution of 0.9 g. of *p*-nitrophenylhydrazine was added. A total of 1.2 g. (56%) of derivative separated, which melted around 157°. After four recrystallizations from methanol the brownish-orange needles melted at 161–162° when immersed at 140°.

*Anal.* Calc'd for $C_{11}H_{13}N_3O_3$: C, 56.1; H, 5.53.
Found: C, 56.09; H, 5.68.

One gram of cut B was hydrolyzed by acid as described above for cut $B_1$. The resulting solution, after five minutes, was neutralized with solid sodium bicarbonate, then a methanol solution of *p*-nitrophenylhydrazine was added. The crude *p*-nitrophenylhydrazone (0.58 g.) melted at 157° after one crystallization. Its mixture m.p. with the 162°-derivative was 159°, demonstrating that it was simply an impure sample of the 162°-derivative.

*Conversion of the 162°- to the 157°-p-nitrophenylhydrazone.* The above derivative of m.p. 162° (0.15 g.) was dissolved in 1.5 ml. of 0.1 *N* methanolic hydrochloric acid, and four drops of water were added to the mixture at its boiling point. Crystals melting at 154° (0.12 g.) separated on cooling. The mixture m.p. of these with the starting material was 135°, but with the derivative melting at 155.5–157° was 155°.

*Ultraviolet absorption spectra.* These are the values for $\lambda_{max.}$ (log $\epsilon$) which are portrayed in Figure 1.

*p*-Nitrophenylhydrazine, 230 (3.85); 384 (4.24).
Tetrahydrofurfural *p*-nitrophenylhydrazone, 249 (3.96); 381 (4.37).
157°-*p*-Nitrophenylhydrazone, 290 (4.03); 400 (4.56).
162°-*p*-Nitrophenylhydrazone, 292 (3.93); 399 (4.52).

*Ozonolysis.* Ozone (0.0140 mole) was passed during 75 minutes into a solution of 2.02 g. (0.0142 mole) of cut B in 150 ml. of carbon tetrachloride. The ozonide was decomposed by shaking it for one hour with 25 g. of warm water and 10 g. of zinc dust. The suspension was filtered. The solvent was distilled off and the aqueous solution was warmed for one hour after the addition of 10 ml. of 10% sodium hydroxide solution and 10 g. of fresh silver oxide. The solution was filtered. Then 10 ml. of syrupy phosphoric acid was added and the volatile acids were distilled with three intermediate additions of water. The 195 ml. of distillate contained a substance which reduced cold neutral permanganate instantly. A 120-ml. aliquot of the distillate was heated for one hour on the steam-bath with 10 g. of mercuric chloride and 10 g. of sodium acetate. The mercurous chloride was collected, washed with hot dilute hydrochloric acid and ethanol, and then dried at 110°. It weighed 2.315 g., from which the molar percentage of formic acid produced was 56.

If any acrylic acid (conceivably formed from IV *via* hydracrylic acid) was present in the above volatile acid, at least it did not interfere with the estimation of formic acid. This was confirmed by treating authentic acrylic acid with mercuric chloride under the conditions given above. There was no formation of mercurous chloride.

In another comparable ozonolysis of 2.0 g. of cut $B_1$ volatile acids were obtained using sulfuric acid instead of phosphoric. The volatile acids were obtained in 250 ml. of distillate. This was shown by titration to contain 0.026 mole of acid. Potassium dichromate (5 g.) and 10 ml. of conc'd sulfuric acid were added to 100 ml. of the distillate and the solution was refluxed for 30 minutes. The solution was then distilled to small residual volume thrice.

Titration of an aliquot showed that the original distillate contained 0.018 mole of nonoxidizable acid and hence 0.0080 mole (57 mole %) of oxidizable acid.

## SUMMARY

Lead tetraacetate reacts with 5,6-dihydro-4*H*-pyran to yield tetrahydro-2-furfurylidene acetate, 5,6-dihydro-4*H*-pyran-4-yl acetate (an ester), and 5,6-dihydro-2*H*-pyran-2-yl acetate (an acylal). Acid hydrolysis of the last of these substances yields 5-hydroxy-2-pentenal from which two isomeric *p*-nitrophenylhydrazones are obtained.

The results are consistent with the postulate of an initial bimolecular reaction, inducing radical formation.

EVANSTON, ILLINOIS

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