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The Reactions of Oximes with Lead Tetraacetate. The Scope of the Reactions

By Yasuhide YUKAWA, Mitsuru SAKAI and Shigeo SUZUKI

The Institute of Scientific and Industrial Research, Osaka University, Sakai, Osaka

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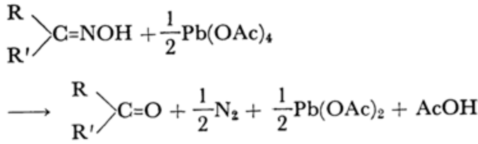
A detailed study of the reaction of oximes by lead tetraacetate has been made. It has been found that the reaction gave nitrogen and the respective aldehydes or ketones in good yields. In the reaction, which can be applied to general oximes, the order of yields was: aliphatic aldoximes >aliphatic ketoximes>alicyclic ketoximes>aromatic ketoximes>aromatic aldoximes. Some limited mechanistic implications are presented and discussed on the basis of the results obtained. Stoichiometrically, it has been found that 2 moles of oxime react with 1 mole of lead tetraacetate to produce 2 moles of aldehyde or ketone and 1 mole of nitrogen.

Many interesting results of the reactions with lead tetraacetate have been observed in a wide variety of organic substrates. In addition to its utility in cleaving glycols and in oxidizing alcohols to aldehydes, lead tetraacetate can be used to introduce methyl or acetoxy groups into suitably-activated positions in organic compounds.[1] More recently, we have found that 1, 2-dioximes could be dehydrogenated and cyclized to form furoxane derivatives quantitatively by adding the dioxime to an acetic acid solution of lead tetraacetate.[2] In the last few years, we have been interested in the reactions of lead tetraacetate, particularly those with olefins and oximes.[3] A thorough search of the literature has revealed that lead tetraacetate-oxime reactions had not previously been investigated in detail. Iffland and Criner,[4] for instance, reported that lead tetraacetate was capable of oxidizing cyclohexanone oxime. Their study was carried out at 0°C for 5 hr. in dichloroethane. They supposed that this reaction product was 1-acetoxy-1-nitrosocyclohexane, but they gave no evidence for this assignment.

In the present paper, we wish to report the results of lead tetraacetate-oxime reaction. The interaction between the two species yields aldehyde or ketone, lead acetate and acetic acid. The scopes, limitations, and synthetic applications of various lead tetraacetate-oxime reactions will be presented in this paper. The kinetic and mechanistic aspects of these reactions will be discussed in a succeeding paper.

Results

The reaction of aldoximes or ketoximes in acetic acid with lead tetraacetate proceeds smoothly, with the evolution of nitrogen, to give the corresponding carbonyl compounds in good yields. The procedure consists of stirring the reactants at 70°C in acetic acid and quenching the reaction mixture by pouring in cold water. A reasonable equation for the over-all reaction seems to be Eq. 1:



$$\begin{matrix}R\\R'\end{matrix}\!\!>\!C{=}NOH + \frac{1}{2}Pb(OAc)_4 \longrightarrow \begin{matrix}R\\R'\end{matrix}\!\!>\!C{=}O + \frac{1}{2}N_2 + \frac{1}{2}Pb(OAc)_2 + AcOH \quad (1)$$

Standard conditions, a one-hour heating at 70°C with a half-equivalent of lead tetraacetate, were employed throughout the present work in order to compare the reactions of different oximes. Product assignments were made by a comparison of the infrared spectra and vapor-phase chromatogram of the products with those of authentic samples. The products were also isolated from the reaction mixture by means of distillation and vapor-phase chromatography. The analytical gas chromatography of nitrogen was performed, using helium as the carrier gas, on a column of Molecular sieve 13X at 25°C.

The reaction was applied to more than thirty oximes of various types. The pertinent data are summarized in Table I.

As is indicated in Table I, seven aliphatic aldoximes, seven aromatic aldoximes, ten aliphatic

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[1] R. Criegee, *Angew. Chem.*, **70**, 173 (1958); G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, **1954**, 3943; R. Criegee, *Ann.*, **481**, 263 (1930); R. F. Brown and L. S. Yee, *J. Am. Chem. Soc.*, **67**, 874 (1945); L. F. Fieser and S. T. Putnum, ibid., **69**, 1038 (1947); L. F. Fieser and E. B. Hershberg, ibid., **60**, 1893, 2542 (1938).

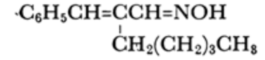
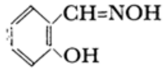
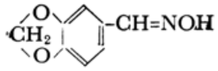
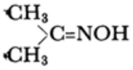
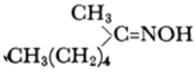
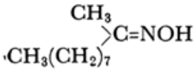
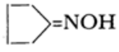
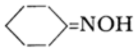
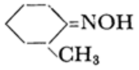
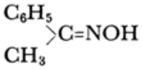
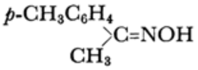
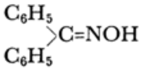
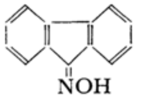
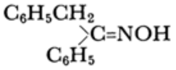
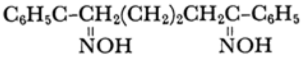
[2] Y. Yukawa and M. Sakai, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **87**, 79, 81, 84 (1966).

[3] Y. Yukawa and M. Sakai, This Bulletin, **36**, 761 (1963).

[4] D. C. Iffland and G. X. Criner, *Chem. & Ind.*, **1956**, 176.

TABLE I. DEOXIMATION BY LEAD TETRAACETATE

Oxime 0.05 mol.; Lead teteaacetate 0.025 mol.; Acetic acid 50 ml.; Temp. 70°C; Time 30 min.

Oxime	M. p., °C	Carbonyl compd. Yield, %
$CH_3(CH_2)_4CH=NOH$	51	69
$CH_3(CH_2)_6CH=NOH$	60	85
$CH_3(CH_2)_7CH=NOH$	63.5	94
$CH_3(CH_2)_8CH=NOH$	67.8	92
$CH_3(CH_2)_9CH=NOH$	71	91
$CH_3(CH_2)_{10}CH=NOH$	72	90
Citral oxime	b. p. 130°C/10 mmHg	75
$C_6H_5CH=NOH$	35	91
p-$CH_3OC_6H_4CH=NOH$	60	90
p-$(CH_3)_2CHC_6H_4CH=NOH$	60	76
$C_6H_5CH=CHCH=NOH$	136	89
 $C_6H_5CH=C(CH_2(CH_2)_3CH_3)CH=NOH$	72	73
	56	46
	115	72
 $(CH_3)_2C=NOH$	59	89
 $CH_3(CH_2)_4C(CH_3)=NOH$	b. p. 110°C/20 mmHg	90
 $CH_3(CH_2)_7C(CH_3)=NOH$	45	91
	56	90
	88	93
	43	91
Camphor oxime	115	None
α-Ionone oxime	89	53
Dihydropseudoionone oxime	b. p. 131°C/3 mmHg	65
Hexahydropseudoionone oxime	b. p. 128°C/3 mmHg	73
Cholestanone oxime	200	75
 $C_6H_5(CH_3)C=NOH$	59	90
 p-$CH_3C_6H_4(CH_3)C=NOH$	86	83
 $(C_6H_5)_2C=NOH$	144	91
	195	89
 $C_6H_5CH_2(C_6H_5)C=NOH$	98	91
 $C_6H_5C(=NOH)-CH_2(CH_2)_2CH_2C(=NOH)-C_6H_5$	232	90

and alicyclic ketoximes and six aromatic ketoximes were readily converted to their corresponding carbonyl compounds in good yields. Therefore, this reaction may be designated as deoximation. Nitrogen was evolved almost quantitatively in every case. It should be noted that the yield of each product in Table I is based on the weight of the pure carbonyl compounds obtained by recrystallization or distillation. In all but a few cases (involving severely-hindered oximes and phenolic hydroxy oximes), deoximation is completed in less than 2 hr. Of special interest was the fact that several aliphatic aldoximes were converted to the aldehydes in high yields. For example, pelargonic aldehyde oxime yielded 94% of the corresponding aldehyde. However, comphor oxime did not undergo any appreciable reaction under the same conditions. This suggests the importance of the steric requirements of the oxime; it was further established by investigating the oxidation of carbomenthone oxime and pulegone oxime in acetic acid at 100°C. Menthone, carbomenthone and pulegone oxime gave blue oils,[5] but no carbonyl compounds. Iffland[4] also isolated a blue material from the reaction of cyclohexanone oxime with lead tetraacetate in the dichloroethane solution at 0°C, he ascribed to this material the structure of 1-acetoxy-1-nitrosocyclohexane. A change in the steric requirements of oximes has a drastic effect on the reaction. The second difficulty of deoximation was encountered in the cases of *o*- and *p*-hydroxyacetophenone, hydroxycitronellal and vanillin oxime. These oximes destroy lead tetraacetate, giving lead dioxide, but the starting oximes were recovered.

TABLE II. CITRAL OXIME DEOXIMATION

Oxime 0.01 mole; Lead tetraacetate 0.005 mole;
Solvent 15 ml.; Temp. 60°C

Solvent	Citral Yield, %
AcOH	75
AcOH+NaOAc (0.01 mol.)	82
C_6H_6	65
C_6H_5Cl	60
Pyridine	45
CH_3CN+Pyridine (0.03 mol.)	57

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[5] The nitroso structure of the blue oils was characterized by a strong nitroso band at 1565 cm^{-1}. The ketones were obtained from this blue material by hydrolyses with 10—20% aqueous hydrochloric acid.

TABLE III. THE OXIDATION OF ACETOPHENONE OXIME BY VARIOUS OXIDANTS

Acetophenone oxime, 0.05 mol.; Oxidants, 0.03 mol.; Solvents, 50 ml.

Oxidant	Solvent	Temp., °C	Time, hr.	Yield, % Acetophenone	Yield, % N_2
Lead tetraacetate	Acetic acid	70	2	92	95
Periodic acid	Dioxane	25	0.5	43	20
Potassium ferricyanide	H_2O-EtOH	60	4	0	0
Sodium bismuthate	Acetic acid	25	0.5	70	60
Mercuric sulfate	Acetic acid	120	2	35	—
Cupric sulfate	Pyridine	80	2	30	15
Potassium dichromate	Acetic acid	80	2	40	45
Mercuric acetate	Acetic acid	80	2	20	5
Cerium nitrate	Acetic acid	25	1	41	20
None	Acetic acid	120	2	1.5	0

The reactions of the unsaturated oximes are interesting because lead tetraacetate can easily attack unsaturated compounds. However the presence of a double bond does not affect the reaction so seriously, though it does lower the yield. It appears to be necessary to choose suitable conditions in such a case. The reaction of citral oxime with lead tetraacetate was investigated under various conditions, which are summarized in Table II.

In these studies, a slight modification of the usual reaction conditions was employed. The best yield of citral (82%) was obtained when acetic acid was used as a solvent and an equivalent mole of anhydrous sodium acetate was added. The yield dropped to 45% when pyridine was employed. In this reaction, lead tetraacetate would act toward oximes as an oxidizing agent, but not as a hydrolyzing agent. It was desirable to compare it with other oxidizing agents. The reactions of acetophenone oxime with periodic acid, potassium ferricyanide, sodium bismuthate, mercuric sulfate, mercuric acetate and cerium nitrate were therefore carried out. The reaction conditions employed and the results obtained are summarized in Table III. Lead tetraacetate and sodium bismuthate were more efficient oxidizing agents than either periodic acid or cerium nitrate. In the absence of an oxidizing agent, only a small percentage of the acetolysis product was obtained. The above results indicated that lead tetraacetate is a suitable oxidizing agent for the conversion of acetophenone oxime to acetophenone.

Experimental

All melting points and boiling points are uncorrected. The melting points were taken on a Yanagimoto melting-point apparatus. The infrared spectra were determined using a Hitachi double-beam spectrophotometer. The vapor-phase chromatographic analyses were carried out on a Yanagimoto Model GCG-3 vapor fractometer. The elemental analyses were performed by the Microanalytical Laboratories of our Institute.

Materials.—The glacial acetic acid was purified with chromium trioxide as before.[6] All of the oximes were prepared in the same manner, using the corresponding carbonyl compounds, hydroxylamine hydrochloride and sodium bicarbonate. The melting points of these oximes are given in Table I.

General Procedure.—Lead tetraacetate was prepared according to the method of Dimroth and Schweizer.[7] It was moistened with acetic acid for storage. The reagent was filtered under suction and dried in a vacuum-desiccator over potassium hydroxide pellets for 6 hr. The resulting white crystalline material was then usually about 98% pure, as estimated by iodometric titration. When reactions were carried out in a solvent other than acetic acid, the lead tetraacetate obtained as above was repeatedly washed with the appropriate solvent and, after filtration, was dried in a vacuum desiccator: in these cases, a brownish material was obtained.

Oximes (0.05 mol.) in glacial acetic acid (30 ml.) was added, drop by drop over a 1 hr. period, to a stirred suspension of lead tetraacetate (0.025 mol.) in glacial acetic acid (20 ml.). The addition of an oxime to lead tetraacetate in acetic acid at room temperature caused an immediate green coloration of the solution. During the addition the reaction mixture was kept at 70°C, and the reaction proceeded rapidly with the evolution of nitrogen. The analytical gas chromatography of nitrogen was performed on a Yanagimoto Model GCG-3, with helium as the carrier gas on a column of Molecular sieve 13X at 25°C. The green reaction mixture gradually turned into a clear yellow solution. After stirring had continued for an additional hour, the solution was poured into ether (50 ml.) and 20 ml. of water was added. The resultant precipitates in the etheral solution had dissolved into the washing water, and no lead dioxide was observed. The etheral layer was washed with 20 ml. of water, six 20 ml. portions of 5% sodium bicarbonate, and two 20 ml. portions of water. The ethereal solution was dried over magnesium sulfate. The ether was removed, and the remaining liquid was distilled through a spinning-band column.

The Reaction of Menthone Oxime with Lead Tetraacetate in Dichloroethane.—To a stirred

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6) E. Berliner and M. C. Beckett, *J. Am. Chem. Soc.*, **79**, 1425 (1957).

7) O. Dimroth and R. Schweizer, *Ber.*, **56**, 1375 (1923).

solution of 3.5 g. (0.021 mol.) of menthone oxime in 50 ml. of dichloroethane, 10.0 g. (0.023 mol.) of lead tetraacetate was added. The temperature was maintained at 0—5°C with cooling. After about 1 hr. of stirring, the solution was deep blue. The resulting mixture was poured into cold water. The dichloroethane layer was separated and dried, and the dichloroethane was evaporated under reduced pressure. The distillation of the residue gave 4.0 g. (85%) of 1-acetoxy-1-nitroso-2-isopropyl-5-methylcyclohexane, b. p. 92°C/3.5 mmHg, $\lambda_{max}^{alc.}$ 680 mμ (ε 18).

Found: C, 63.62; H, 9.70. Calcd. for $C_{12}H_{21}NO_3$; C, 63.41; H, 9.31%.

We wish to thank the Shiono-koryo Company for the kindness of providing us with samples of citral, menthone, carbomenthone and pulegone. We are also indebted to Mr. Tsuneyo Shishido and Takuzo Fujino of the Microanalytical Section of this laboratory for microanalyses.