Asp or Asn from PC-1 or any of the peptides containing position 3. This difficulty was overcome by a CoB digestion of C16A which gave the peptides A,B1, A,B2, A,B3, and A,B4 along with Val, AECys, Ser, Thr, and Leu. A,B4 was shown to result from a "chymotryptic-like" split at bond 4–5. Since peptide A,B1 involved positions 1–3 it proved suitable for its Edman study. Two cycles of Edman degradation released Asn from position 3. (3) Extended digestion of CNBr-1 with LAP released Gly, Phe, Glu, traces of Pro, and H-Gly-Pro-OH. A good yield of Glu (0.9 mole) and no release of Gln established Glu at position 30. (4) Prolinamide (Pro-NH$_2$) at position 32 was established by its release after the sixth Edman degradation cycle on peptide CNBr-1 (identified as DNS-Pro-NH$_2$ and also as H-Pro-NH$_2$).

Details of the purification, structure, and enzyme digestion restrictions such as those imposed by the N-terminal disulfide ring of PC-1 will be reported in two publications now in preparation.[14]

[14] Preliminary studies, designed to synthesize PC-1, by G. W. Anderson, F. M. Callahan, A. E. Lanzilotti, and J. E. Zimmerman of these laboratories have given material with hypocalcemic activity. Synthetic work will be reported later.

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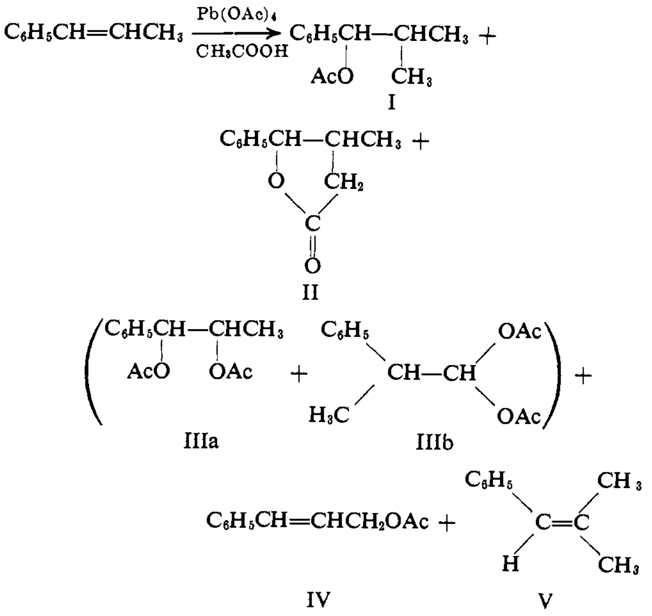
Oxidation by Metal Salts. II. The Formation of γ-Lactones by the Reaction of Lead Tetraacetate with Olefins in Acetic Acid[1]

Sir:

Criegee, in a recent review article, mentioned a peculiar reaction in which a γ-lactone was obtained as a side product from the reaction of lead tetraacetate with octene-4 in acetic acid.[2] The γ-lactone was only observed with octene-4 and the mechanism of the reaction leading to this lactone was unknown.

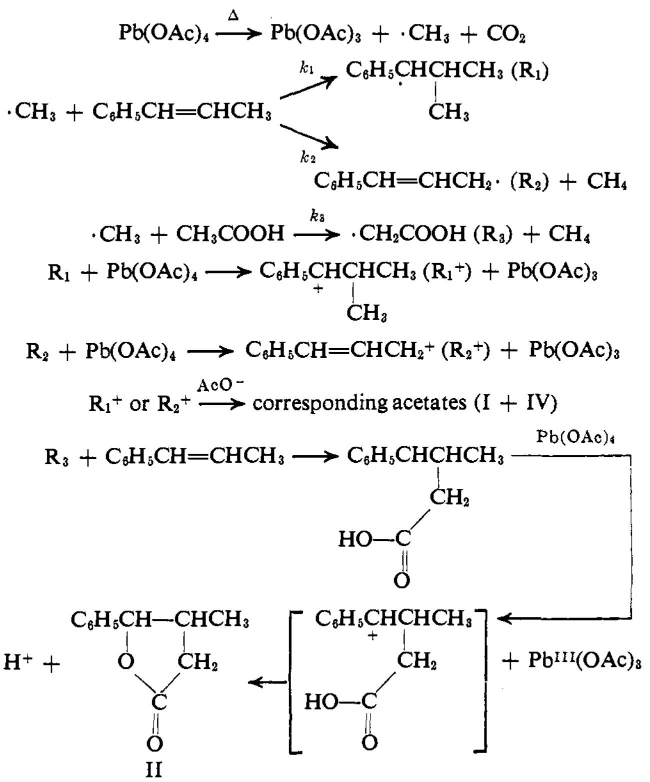
We wish to report our results, which indicate the generality of this reaction in that γ-lactones have been obtained by the reaction of lead tetraacetate with octene-1, styrene, and β-methylstyrene. We also wish to present a mechanism which explains the formation of these lactones and which predicts the conditions conducive to their formation.

We studied the reaction of lead tetraacetate with *trans*-β-methylstyrene in refluxing acetic acid in some detail. In the presence of added anhydrous potassium acetate (approximately 1 *M* or greater) and low olefin concentrations (0.2 *M* or less) under a nitrogen atmosphere, two major products were obtained. These were identified as the methyl acetate adduct I and the lactone II on the basis of their nmr and infrared spectra and elemental analyses. In addition to these two major products, we isolated a mixture of diacetates, consisting of 65% *threo*- and *erythro*-1,2-diacetates (IIIa) and 35% rearranged 1,1-diacetate (IIIb), together with some allylic acetate IV and traces of the olefin V.



In a typical experiment, *trans*-β-methylstyrene (35 mmoles) and lead tetraacetate (4.2 mmoles) were refluxed in 100 ml of glacial acetic acid containing 30 g of anhydrous potassium acetate[3] under a nitrogen atmosphere. The following products were obtained: methyl acetate adduct I (1.91 mmoles), lactone II (0.80 mmole), diacetates III[4] (0.36 mmole), allylic acetate IV (0.4 mmole), and the olefin V (0.04 mmole),

Scheme I



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[1] Previous article in this series: E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, 90, 1082 (1968).

[2] R. Criegee in "Oxidation in Organic Chemistry," Part A, K. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, p 277.

[3] The large concentration of potassium acetate was used to increase the temperature of the refluxing solution to 138°.

[4] The formation of diacetates in the oxidation of styrene with lead tetraacetate was attributed to an ionic mechanism by R. O. C. Norman and C. B. Thomas, *J. Chem. Soc., B*, 771 (1967). This explanation is in accord with our results, which indicate that the yield of the diacetate can be suppressed by the addition of potassium acetate and high reaction temperatures.

thereby accounting for 83% of the lead tetraacetate used. The relative yield of the γ-lactone II to the methyl acetate adduct I was found to vary with changes in the acetic acid/olefin ratio as shown in Figure 1. This is consistent with the free-radical chain mechanism[5] shown in Scheme I. The chain propagates *via*

$$Pb^{III}(OAc)_3 \longrightarrow Pb^{II}(OAc)_2 + \cdot CH_3 + CO_2$$

and terminates *via*

$$Pb^{III}(OAc)_3 + R_1, R_2, \text{ or } R_3 \longrightarrow (R_1\ R_2, \text{ or } R_3)^+ + Pb^{II}(OAc)_2 + AcO^-$$

In the proposed mechanism of Scheme I it is assumed that $\cdot CH_3$ and $\cdot CH_2COOH$ radicals are not readily oxidized to the corresponding carbonium ions, in contrast to the benzylic radical which should be rapidly oxidized,[6] owing to their relatively high ionization potentials.[7]

The linear dependence of the lactone/methyl acetate adduct ratio on the acetic acid/olefin ratio is consistent with our proposed mechanism, in which a free methyl radical reacts either with the olefin or with the acetic acid.[8]

The allylic acetate IV is formed predominantly *via* hydrogen abstraction by methyl radical and not by the stable $\cdot CH_2COOH$ radical as indicated by the finding that the allylic acetate IV consistently represents approximately one-fifth of the methyl acetate adduct I formed irrespective of the relative ratio of I to II (*i.e.*, $k_1/k_2 \simeq 5$).[9]

Our proposed free-radical mechanism is substantiated by the finding that ultraviolet irradiation (3500 Å) at 25° yielded the same products I and II, while no reaction was observed at this temperature in the absence of light. The ratio of II/I in the photochemical reaction depended on the HOAc/olefin ratio used, just as had been observed in the thermal reaction (Figure 1).

From the slopes in Figure 1, the relative rate constants k_1/k_3 were found to be 130 for the thermal reaction at 138° and 290 for the photochemical reaction at 25°. The activation energy difference for methyl radical abstraction *vs.* addition, $E_3 - E_1$, as determined from these two slopes was equal to 1.7 kcal/mole. An identical value was obtained by comparison of thermal reactions performed at 80 and 138°.

The formation of γ-lactones as well as methyl acetate adducts was observed with all the olefins studied; namely, styrene, *trans*- and *cis*-β-methylstyrene, and octene-1. From the ratio of methyl acetate adduct/lactone obtained with various olefins, when the oxidation with lead tetraacetate was carried out under identical experimental conditions, it was possible to calculate the relative reactivity of these olefins toward the addition of methyl radicals.

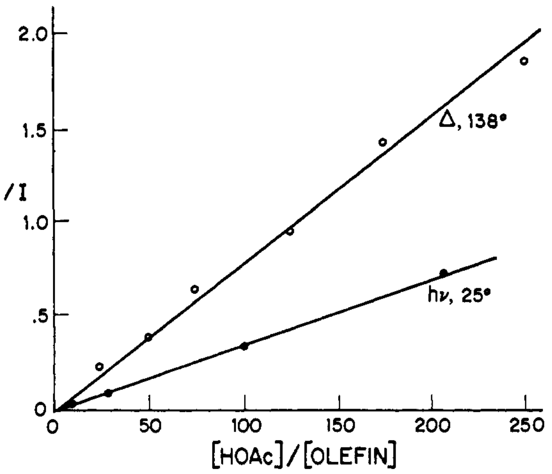

Figure 1. Effect of acetic acid/olefin ratio on the product ratio II/I.

The relative reactivities at 138° so obtained were as follows: styrene (12), *trans*-β-methylstyrene (1), *cis*-β-methylstyrene (0.33), and octene-1 (0.14). The order of reactivity agrees well with that reported for methyl radical generated in other ways.[10]

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[5] The free-radical nature of the reaction is indicated by the fact that the relative yield of I and II is decreased upon the addition of oxygen or radical inhibitors such as 4-*t*-butylcatechol.

[6] J. J. Kochi, J. D. Bacha, and T. W. Bethea, *J. Am. Chem. Soc.*, 89, 6538 (1967).

[7] The gas-phase IP of $\cdot CH_3$ = 9.83 eV, and the IP of $\cdot CH_2COOH$ is expected to be similar to that of cyanomethyl radical whose IP = 10.87 eV, while that of the benzylic radical is 7.76 eV: R. W. Kaiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 319.

[8] Norman and Thomas[4] proposed that formation of the methyl acetate adduct in the reaction of styrene with $Pb(OAc)_4$ is initiated by molecule-induced homolysis involving no free methyl radicals.

[9] From our studies with toluene[1] we have found that $k_{\text{addition}}/k_{\text{abstraction}}$ for $\cdot CH_2COOH$ is considerably larger than that for methyl radical. Therefore one might expect the ratio of k_1/k_2 for $\cdot CH_2COOH$ to be quite large, so that only addition is observed with β-methylstyrene.[1]

[10] F. Carrock and M. Szwarc, *J. Am. Chem. Soc.*, 81, 4138 (1959), reported relative reactivities of styrene (9), *trans*-β-methylstyrene (1), *cis*-β-methystyrene (0.43), and propylene (0.25) at 65° using acetyl peroxide and isooctane as a solvent. Considering the temperature difference, our values appear to indicate that methyl radical generated from $Pb(OAc)_4$ in acetic acid containing $Pb(OAc)_4$ is somewhat more selective. This difference in selectivity may be attributed to either a solvent effect or to the possible complexing of methyl radicals with either Pb^{III} or Pb^{II} generated during the course of the reaction.

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Five-Coordinate Complexes of Platinum(II) and Palladium(II)

Sir:

Square-planar complexes of iron group elements are thought to undergo ligand substitution by a mechanism which involves the formation of five-coordinate species either as an activated complex or a metastable intermediate.[1] No direct evidence has appeared to substantiate the formation of the metastable intermediate with platinum or palladium complexes, but numerous examples of crystalline five-coordinate iron group complexes[1-3] are known.

We report here direct nuclear magnetic resonance spectral evidence for five-coordinate complexes formed as intermediates. Adduct formation clearly precedes ligand substitution in reactions of xanthates and dithiocarbamates of palladium(II) and platinum(II) with methyldiphenylphosphine.

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[1] F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 376; L. Cattalini, A. Orio, and M. L. Tobe, *J. Am. Chem. Soc.*, 89, 3130 (1967).

[2] R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stollberg, *ibid.*, 87, 658 (1965).

[3] See, for example, E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), 20, 245 (1967).