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The Oxidation of Chloromethyl Compounds with Lead Tetraacetate

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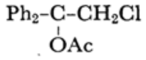
In studying the reaction of styrene, olefins, vinyl ethers and vicinally-substituted compounds with lead tetraacetate, it was shown that the methyl group of 9-chloro-9-methylfluorene was easily acetoxylated with lead tetraacetate. This novel reaction was then applied to 1, 1-diphenylethyl chloride, 1-phenylethyl chloride and *t*-butyl chloride. In every case the methyl group of chlorides with an α-methyl group was acetoxylated preferentially.

The authors have, in recent years, been studying the reactions of lead tetraacetate with various unsaturated compounds, such as styrene, olefins, vinyl ethers and vicinally-substituted compounds.[1] In this paper we wish to report the novel acetoxylation of a methyl group with lead tetraacetate. It has been found that the methyl group of 9-chloro-9-methylfluorene, 1, 1-diphenylethyl chloride, 1-phenylethyl chloride and *t*-butyl chloride is preferentially acetoxylated by the reactions with lead tetraacetate. Table I shows the results of these reactions.

The yield of the acetoxylated products has been slightly raised by the addition of a small amount of anhydrous sodium acetate. The formation of tarry by-products has been suppressed when the reaction is carried out at a moderate temperature, below 70°C.

The lead tetraacetate could be used without any special precautions for its purification, since it has been found that these acetoxylation reactions are not influenced by the presence of the 10 to 15% of lead dioxide which could be a major impurity of lead tetraacetate.

The structures of the products were assigned by their conversion to the respective glycols. The hydrolysis of the 2-chloro-acetate was carried out by sodium hydroxide in methanol. The resulting glycols were shown to be III, VI, IX and XII by a comparison of these infrared spectra and the retention times in gas chromatography (on two different columns, silicon grease and apiezon grease on firebrick) with those of the authentic samples. The migration of the chlorine atom was rejected in the oxidation of IV. The structures for the two isomers of V and XIII were assigned by Summerbell.[2] The melting points of V and XIII were 76 and 30°C respectively. XIII was synthesized from ethyl chloroacetate and phenylmagnesium bromide, followed by acetylation with acetic anhydride. The product in the oxidation of IV showed a marked depression of melting point when mixed with XIII.

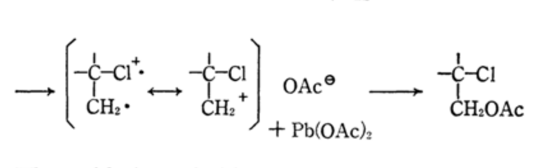


$$\underset{\textstyle \mathrm{OAc}}{\mathrm{Ph_2\text{-}C\text{-}CH_2Cl}}$$

(XIII)

Neither 2-phenylethyl halide nor cyclohexyl halide was acetoxylated, even under more drastic conditions. Bromides with an α-methyl group gave similarly acetoxylated products. Iodides gave mainly tarry products. Thus it has been demonstrated that chlorides and bromides in which the methyl group and halogen atoms are joined to the same carbon atom react with lead tetraacetate to give halohydrin acetates in fairly good yields.

Although the mechanism of this reaction has not yet been settled, there can be little doubt, in view of the radical mechanism in lead tetraacetate oxidation, that the reaction involves a one electron-transfer from chlorine to lead (Pb^{IV}) and a concurrent hydrogen abstraction from the methyl group by an acetoxyl radical. The following mechanism is tentatively suggested:



The oxidation of chloromethyl compounds with lead tetraacetate in acetic acid provides a useful route for the synthesis of pure chlorohydrin acetate.

Experimental

The melting points were determined on a Yanagimoto hot bench melting point apparatus and are corrected. The elementary analyses were performed by the Microanalytical Laboratories of Osaka University. The

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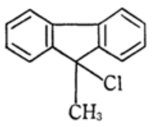
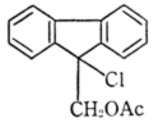
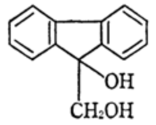
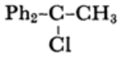
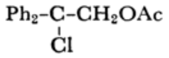
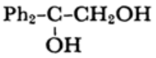
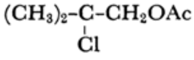
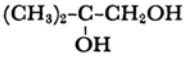
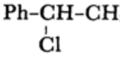
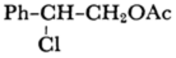
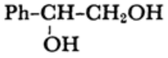
[1] Y. Yukawa and M. Sakai, This Bulletin, **36**, 761 (1963); Y. Yukawa and M. Sakai, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **87**, 79, 81, 84 (1966).

[2] R. K. Summerbell and M. J. Kland-English, *J. Am. Chem. Soc.*, **77**, 5095 (1955).

TABLE I. THE REACTION BETWEEN α-METHYL CHLORIDES AND LEAD TETRAACETATE

Starting material	Product	Yield	Glycol
 (I)	 (II)	50%	 (III)
 $Ph_2\text{-}\underset{Cl}{C}\text{-}CH_3$ (IV)	 $Ph_2\text{-}\underset{Cl}{C}\text{-}CH_2OAc$ (V)	50%	 $Ph_2\text{-}\underset{OH}{C}\text{-}CH_2OH$ (VI)
$(CH_3)_3\text{-}C\text{-}Cl$ (VII)	 $(CH_3)_2\text{-}\underset{Cl}{C}\text{-}CH_2OAc$ (VIII)	45%	 $(CH_3)_2\text{-}\underset{OH}{C}\text{-}CH_2OH$ (IX)
 $Ph\text{-}\underset{Cl}{CH}\text{-}CH_3$ (X)	 $Ph\text{-}\underset{Cl}{CH}\text{-}CH_2OAc$ (XI)	45%	 $Ph\text{-}\underset{OH}{CH}\text{-}CH_2OH$ (XII)

infrared spectra were determined using a Hitachi double-beam spectrophotometer.

Materials.—Lead tetraacetate was prepared from red lead oxide and acetic acid.[3] The following reagents were commercial materials and were redistilled before use; acetic acid, butanol, *t*-benzaldehyde, β-phenylethyl alcohol and ethyl chloroacetate. The following commercial reagents were used without further purification; benzophenone, fluorenone, cyclohexanol and methyl iodide. 9-Chloro-9-methylfluorene,[4] 1, 1-diphenylethyl chloride,[5] *t*-butyl chloride[6] and 1-phenylethyl chloride[7] were prepared by the methods described in the literature.

General Procedure.—In order to avoid needless repetition, the experimental conditions for carrying out these reactions have been generalized. A stirred solution of 0.1 mol. of the substituted chloride and 0.1—0.12 mol. of lead tetraacetate in 100 ml. of a solvent, under a slight pressure of dry nitrogen, was maintained at 60 to 70°C for about 0.5—1 hr. From the resulting clear solution, about a half of the acetic acid was removed under a vacuum below 65°C. The residue was then dissolved in ethyl ether (100 ml.) and washed with water (80 ml.) three times in order to remove the inorganic lead compounds. The etheral solution was treated with anhydrous sodium sulfate filtered, and vacuum-distilled.

9-Acetoxymethyl-9-chlorofluorene (II).—Under the general procedure, with acetic acid as the solvent, 9-chloro-9-methylfluorene and lead tetraacetate gave a 50% yield of II, m. p. 118°C (from ethanol).

Found: C, 70.17; H, 4.76; Cl, 13.16. Calcd. for $C_{16}H_{13}O_2Cl$: C, 70.46; H, 4.80; Cl, 13.00%.

The hydrolysis of II gave 9-hydroxymethyl-9-fluorenol (III), m. p. 105—106°C (from benzene), lit.[8] m. p. 105—108°C.

Found: C, 79.31; H, 5.84, Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

2-Chloro-2, 2-diphenylethyl Acetate (V).—Under the general procedure, with acetic acid as the solvent, 1, 1-diphenylethyl chloride and lead tetraacetate gave a 50% yield of V, m. p. 75—76°C (from ethanol).

Found: C, 69.85; H, 5.61; Cl, 13.07. Calcd. for $C_{16}H_{15}O_2Cl$: C, 69.95; H, 5.50; Cl, 12.90%.

The hydrolysis of V gave asym-diphenylethylene glycol (VI), m. p. 122°C (from benzene); lit.[9] m. p. 121°C.

2-Chloro-2, 2-dimethylethyl Acetate (VIII).—Under the general procedure, with acetic acid as the solvent, *t*-butyl chloride and lead tetraacetate gave a 45% yield of VIII, b. p. 95—97°C/35 mmHg.

Found: Cl, 23.83. Calcd. for $C_6H_{11}O_2Cl$: Cl, 23.54%.

The hydrolysis of VIII gave asym-dimethylethylene glycol (IX) (diphenylurethan, m. p. 140°C).

2-Chloro-2-phenylethyl Acetate (XI).—Under the general procedure, with acetic acid as the solvent, 1-phenylethyl chloride and lead tetraacetate gave a 45% yield of XI, b. p. 110°C/4.0 mmHg.

Found: Cl, 17.54. Calcd. for $C_{10}H_{11}O_2Cl$: Cl, 17.85%.

The hydrolysis of XI gave styrene glycol (XII), m. p. 67°C.

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[3] O. Dimroth and R. Schweizer, *Ber.*, **56**, 1375 (1923).

[4] H. Wieland, *Ann.*, **433**, 135 (1925).

[5] S. Kawamatsu, K. Oikawa and T. Inoue, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kōgyō Kagaku Zassi*), 53 **357** (1950).

[6] H. Stone and H. Shechter, *J. Org. Chem.*, **15**, 491 (1950).

[7] G. L. Goerner and W. G. Hines, *J. Am. Chem. Soc.*, **70**, 3511 (1948).

[8] T. Mole, *J. Chem. Soc.*, **1960**, 2132.

[9] F. N. Peters, Jr., and E. Griffith, *J. Am. Chem. Soc.*, **47**, 453 (1925).