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The Reaction of *p*-Methoxystyrene-α-^{14}C with Lead Tetraacetate

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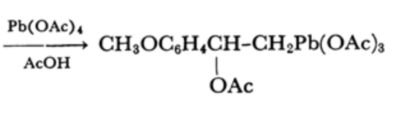
The reaction of *p*-methoxystyrene with lead tetraacetate in glacial acetic acid should proceed mainly through the rearrangement of the carbon skeleton. The possibility of the hydrogen migration can not be ruled out, but its extent should be only 7% even if it is involved.

It has been known that lead tetraacetate is an effective oxidizing reagent not only for the fission of 1, 2-glycols, but also for the introduction of acetoxy groups into unsaturated compounds. The mechanism of the reaction of lead tetraacetate on the olefinic compounds is not so straightforward. There is a considerable variation in the products depending on the olefin used and on the conditions of the reaction. The normal reaction should be the addition of two acetoxy groups to a carbon-carbon double bond, but an abnormal reaction giving the rearranged product has usually been observed.

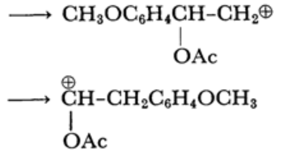
Criegee et al.[1] reported that the reaction of *p*-methoxystyrene in glacial acetic acid with lead tetraacetate gave *p*-methoxyphenylacetaldehyde diacetate. The most plausible mechanism of this reaction is the 1, 2-nucleophilic rearrangement of the *p*-anisyl group, as has been suggested by Criegee:

$CH_3OC_6H_4CH{=}CH_2$

(I)



$$\xrightarrow[AcOH]{Pb(OAc)_4} CH_3OC_6H_4\underset{\substack{|\\ OAc}}{C}H\text{-}CH_2Pb(OAc)_3$$



$$\longrightarrow CH_3OC_6H_4\underset{\substack{|\\ OAc}}{C}H\text{-}CH_2{\oplus}$$

$$\longrightarrow \underset{\substack{|\\ OAc}}{\overset{\oplus}{C}}H\text{-}CH_2C_6H_4OCH_3$$

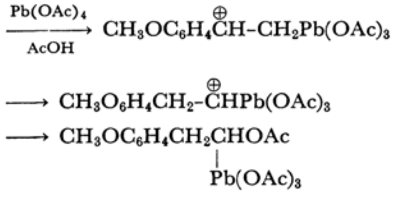
$$\longrightarrow (AcO)_2CH\text{-}CH_2C_6H_4OCH_3$$

(II)

However, it can just as well be explained by the 1, 2-migration of hydrogen. The following mechanisms may, therefore, be suggested:

$CH_3OC_6H_4CH{=}CH_2$

(I)



$$\xrightarrow[AcOH]{Pb(OAc)_4} CH_3OC_6H_4\overset{\oplus}{C}H\text{-}CH_2Pb(OAc)_3$$

$$\longrightarrow CH_3O_6H_4CH_2\text{-}\overset{\oplus}{C}HPb(OAc)_3$$

$$\longrightarrow CH_3OC_6H_4CH_2\underset{\substack{|\\ Pb(OAc)_3}}{C}HOAc$$

$$\longrightarrow CH_3OC_6H_4CH_2CH(OAc)_2$$

(II)

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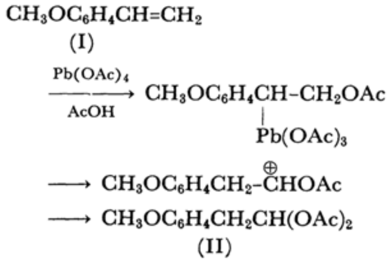
[1] R. Criegee, P. Dimroth, K. Noll, R. Simons and C. Weis, *Chem. Ber.*, **90**, 1070 (1957).



$$\underset{\text{(I)}}{CH_3OC_6H_4CH{=}CH_2} \xrightarrow[\text{AcOH}]{\text{Pb(OAc)}_4} CH_3OC_6H_4\underset{\text{Pb(OAc)}_3}{\underset{|}{CH}}{-}CH_2OAc \longrightarrow CH_3OC_6H_4CH_2{-}\overset{\oplus}{C}HOAc \longrightarrow \underset{\text{(II)}}{CH_3OC_6H_4CH_2CH(OAc)_2}$$

In the present paper, the confirmation of the actual migrating group by means of the carbon-14 tracer technique will be reported.

It was found that styrene itself gives phenylacetaldehyde diacetate with lead tetraacetate in acetic acid. However, *p*-methoxystyrene was selected as the starting material in view of the powerful migrating aptitude of the *p*-anisyl group and the experimental convenience of the separation and purification of the reaction product. *p*-Methoxystyrene-α-^{14}C (I) was obtained, through *p*-anisaldehyde-carbonyl-^{14}C, from *p*-anisic acid-carbonyl-^{14}C, which had been prepared from *p*-methoxyphenyl magnesium bromide and carbon dioxide-^{14}C.

The treatment of *p*-methoxystyrene-α-^{14}C with lead tetraacetate in glacial acetic acid gave *p*-methoxyphenylacetaldehyde-diacetate-^{14}C, namely, 2-methoxyphenylethyl-1, 1-diol diacetate-^{14}C (II), as white needles. The specific radioactivity of II was 2.53 μc./mmol.

On the oxidation of II with an aqueous solution of potassium permanganate, followed by acidification, the fission products, carbon dioxide and anisic acid, were obtained. The specific activity of the carbon dioxide was 2.15 μc./mmol., which corresponds to 85% of the activity of the reaction product, II. This indicates that the rearrangement of the anisyl group is the major process of the reaction. The specific activity of anisic acid was 0.16 μc./mmol. This corresponds to 6.7% of the activity of II, suggesting the rearrangement of anisyl group up to 93.3%. The decrease in the activity of the carbon dioxide can be attributed to the formation of low-activity carbon dioxide by the further oxidation of anisic acid by permanganate. The activity of the anisic acid suggests hydrogen migration to a maximum extent of 7%.

In conclusion, the reaction of *p*-methoxystyrene with lead tetraacetate in glacial acetic acid should proceed mainly through the rearrangement of the carbon skeleton. The possibility of the hydrogen migration can not be ruled out, but its extent should be only 7% even if it is involved.

Experimental

The Preparation of *p*-Methoxystyrene-α-^{14}C.—*p*-Anisic acid-carboxyl-^{14}C was prepared by the Grignard carboxylation of *p*-bromoanisole (15 mmol.) with carbon dioxide liberated from barium carbonate (10 mmol.) (labeled: 1 mc./8.5 mg; unlabeled; 1.97 g.) by the usual method.2) The acid was obtained in a 60% yield, m. p. 182—183°C; 0.9 g. The specific radioactivity was determined to be 90 μc./mmol.; total activity 533 μc. by the Van-Slyke-Folch wet combustion method.3)

The labeled anisic acid was converted into the acid chloride with thionyl chloride, and the chloride was reduced to the aldehyde by the Rosenmund method. The resultant aldehyde, diluted to 15 g. with the unlabeled aldehyde, was then added to the Grignard solution from 17 g. of methyl iodide. This mixture was allowed to stand overnight and decomposed with ice and diluted sulfuric acid. The ethereal layer was separated, dried, and evaporated. On the distillation of the residue, 7.4 g. of the styrene (I), b. p. 92—97°C/16 mmHg was obtained.

The Reaction of *p*-Methoxystyrene with Lead Tetraacetate.—*p*-Methoxystyrene-α-^{14}C (2.7 g.) was added to a suspension of 10 g. of lead tetraacetate in 20 ml. of acetic acid. The mixture was then stirred for 2 hr. at room temperature and poured onto ice water. The oil which separated was taken up into ether, and the solvent was evaporated. The residue was solidified on keeping it in an ice-box and recrystallized from petroleum ether, giving fine needles of II, m. p. 49—50°; 1.9 g. The specific activity of the II obtained was 2.53 μc./mmol.

The diacetate II (0.4 g.) was oxidized in the usual manner by boiling it for 2 hr. in an aqueous acetone solution of alkaline potassium permanganate. After the manganese dioxide was been removed by filtration, the filtrate was acidified and the carbon dioxide liberated was absorbed into a barium hydroxide solution. The barium carbonate obtained showed a specific activity of 2.15 μc./mmol. By ether extraction, 0.1 g. of the anisic acid was obtained from the above acidified filtrate. The specific activity of this product was 0.16 μc./mmol.

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2) A. Murray, III, and D. L. Williams, "Org. Synth. with Isotopes," Part I, Interscience Publishers, New York (1958), p. 86.

3) D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **136**, 509 (1940); D. D. Van Slyke, J. Plazin and J. R. Weisiger, ibid., **191**, 299 (1951).