it was refluxed for an additional hour, cooled and filtered. The precipitate of *sym*-diphenylurea was washed with ether and weighed. The dark brown ether solution was distilled *in vacuo*. The nitroalkane was recovered and the yellow furoxane was obtained. The details of each experiment are summarized in Table II.

The same results were obtained when tri-*n*-butylamine was used instead of triethylamine.

Reaction of *p*-Nitrophenylnitromethane and Phenyl Isocyanate.—A solution of *p*-nitrophenylnitromethane (3.3 g., 0.018 mole) and phenyl isocyanate (4.3 g., 0.036 mole) in 200 ml. of dry ether in the presence of 10 drops of triethylamine was heated to reflux for 6 hours to give *sym*-diphenylurea, 3.1 g. (80% of theoretical) and a dark brown resinous material instead of an expected di-*p*-nitrophenylfuroxane. This resinous material may be a polymer of *p*-nitrobenzonitrile oxide.

Reaction of 1-Nitropropane with Ethyl Isocyanate.—A solution of 1-nitropropane (6.3 g., 0.07 mole) and ethyl isocyanate (5.0 g., 0.07 mole) in 15 ml. of dry ether in the presence of 10 drops of triethylamine was heated under reflux for 55 hours to give *sym*-diethylurea, 3.1 g. (77.5% of theoretical), m.p. 108–110°, and diethylfuroxane, b.p. 109–110°(10 mm.), 1.6 g. (64% of theoretical). The 1-nitropropane, 1.3 g., was recovered.

Reduction of Dimethylfuroxane and Diethylfuroxane.—Dimethylfuroxane (2.7 g.), diluted with 40 ml. of 95% ethanol, was reduced by hydrogen under atmospheric pressure in the presence of Raney nickel at room temperature. It absorbs 1 mole of hydrogen in 5 hours. On evaporating the reaction mixture under reduced pressure, 0.15 g. of the red ether-insoluble product, $C_8H_{14}N_4O_4Ni$, and 1.4 g. of the ether-soluble product, $C_4H_8N_2O_2$, were obtained. The latter melted at 109–111°, solidified at an elevated temperature and remelted at 231–232°. The resolidified material was identical with α-dimethylglyoxime and showed no depression in mixed melting point with an authentic sample. The product melting at 109° may therefore be considered to be the γ-isomer of dimethylglyoxime.

Anal. Calcd. for $C_8H_{14}N_4O_4Ni$: N, 19.37. Found: N, 19.13. Calcd. for $C_4H_8N_2O_2$: C, 41.37; H, 6.94; N, 24.13. Found: C, 41.54; H, 6.97; N, 23.96.

Using the procedure described above, the reduction of 2.0 g. of diethylfuroxane gave 1.2 g. of hydrogenated product, $C_6H_{12}N_2O_2$, m.p. 90–92° recrystallized from benzene. It solidified also at an elevated temperature and remelted at 185–186° with partial sublimation. The resolidified material was identical with α-diethylglyoxime and showed no depression in mixed melting point with an authentic sample. The product melting at 90° may therefore be considered to be the γ-isomer of diethylglyoxime.

Anal. Calcd. for $C_6H_{12}N_2O_2$: C, 49.98; H, 8.39; N, 19.43. Found: C, 50.10; H, 8.35; N, 19.30.

Preparation of 3-Methyl(ethyl)isoxazolines and Oxadiazolines.—To 25 ml. of dry benzene containing 0.1 mole of phenyl isocyanate and 0.055 mole of unsaturated compound (Table I) was added to a solution of 0.055 mole of nitroethane (1-nitropropane) and 10 drops of triethylamine in 15 ml. of dry benzene. The reaction started, evolving carbon dioxide, and *sym*-diphenylurea precipitated. After shaking the reaction mixture for 1 hour, it was refluxed for an additional hour, cooled and filtered. The brownish-yellow benzene solution was then distilled and the liquid products were distilled under reduced pressure. The crystalline products obtained in the case of vinyl acetate were recrystallized from 95% ethanol. The yield of *sym*-diphenylurea and the yields, boiling points (melting points) and analyses for isoxazolines and oxadiazolines are listed in Table I.

Preparation of 3-Methyl(ethyl)isoxazoles.—By heating 14.3 g. of 3-methyl-5-acetoxyisoxazoline above 170° under atmospheric pressure, products boiling at 115–118° were obtained. They were taken up in ether and washed successively with a small amount of dilute sodium hydroxide solution and water, dried over calcium chloride, and distilled. 3-Methylisoxazole, C_4H_5NO, 5.2 g. (62.6% of theoretical), b.p. 114–114.5°, was obtained.

Anal. Calcd. for C_4H_5NO: C, 57.82; H, 6.07. Found: C, 57.40; H, 6.15.

Using the procedure described above, 3-ethyl-5-acetoxyisoxazoline decomposed at 160° and gave 3-ethylisoxazole, C_5H_7NO, b.p. 130–131°.

Anal. Calcd. for C_5H_7NO: C, 61.84; H, 7.27. Found: C, 61.2; H, 7.70.

Acknowledgments.—The authors express their hearty thanks to Mr. Shigetaka Mitsui and Miss Etsuko Sakata for their assistance during the course of this experiment and to Mr. Asaji Kondo for the microanalyses.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE, NEWARK, DEL.]

The Oxidation of Aliphatic Esters with Lead Tetraacetate[1]

BY WILLIAM A. MOSHER AND CLIFTON L. KEHR

RECEIVED JANUARY 26, 1960

A novel reaction of lead tetraacetate resulting in acetoxylation of the alcoholic component of aliphatic esters has been investigated. A study of the products shows that an ionic mechanism involving methyl carbonium ions readily explains the course of the reaction. These results supplement previously reported evidence that lead tetraacetate is capable of functioning as an ionic reagent in oxidation reactions.

During an investigation[2] of the oxidation of organic acids with lead tetraacetate, it was noted that in the case of the lower aliphatic acids the material balances of the oxidation reactions were quite low. Because the lead tetraacetate was nevertheless invariably completely reduced, it became apparent that one or more of the initial reaction products was being attached by the oxidizing agent to give products too complex to isolate. The presence of small amounts of esters among the products of these reactions led to the present investigation. A summary of the products of the unique reaction of lead tetraacetate with esters is given along with pertinent reaction conditions in Table I (in each case glacial acetic acid was used as the solvent).

The course of the reaction of lead tetraacetate with the above esters apparently proceeds initially through the acetoxylation of the α-carbon atom of the alcoholic component of the ester. In each reaction studied the ester was used in excess of the required molar amount in order to ensure that a favorably high concentration be present even toward the end of the reaction. In spite of this precaution, however, the yields of any one product obtained were quite low. This is undoubtedly true because the product itself is a much better

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[1] Presented in part before the Division of Organic Chemistry, American Chemical Society, Kansas City, Mo., April, 1954.

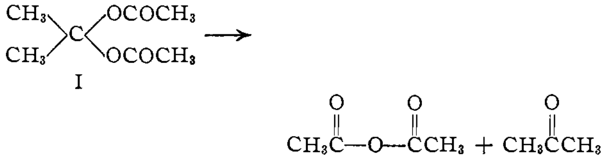
[2] W. A. Mosher and C. L. Kehr, THIS JOURNAL, **75**, 3172 (1953).

TABLE I

Reactant	CO_2, %	Other products, %	Conditions Time, hr.	Conditions T, °C.
Isopropyl acetate	44.7	Acetic anhydride, 19.5	7	114
n-Butyl *n*-butyrate	44.1	1-Acetoxy-1-butyroxy-butane, 11.6 Diacetoxybutyroxy-butane, 12.8	11	129
n-Propyl acetate	53.5	Propylidene diacetate, 25.0	12	119
Methyl acetate	69.7	Methylene diacetate, 2.6	35	110–125
Acetic acid[3]		Methyl acetate, 1.3	26	122

reducing agent than the starting material. Consequently, as the concentration of the primary product increases, it is preferentially attacked and destroyed by the remaining lead tetraacetate.

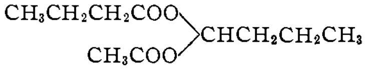
Of the compounds investigated, isopropyl acetate was found to be the most reactive. This is believed to be a result of the fact that the hydrogen atom at the point of attack is tertiary and, consequently, quite labile. The expected acetoxylated product I is apparently unstable[4] and decomposes instantly



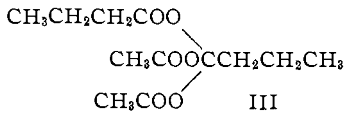
I

Acetic anhydride[5] was isolated in 19.5% yield. The absence of acetone in the reaction products is not disturbing, as Dimroth and Schweizer[5] have shown that it is rather rapidly attacked by lead tetraacetate and we have confirmed this fact.

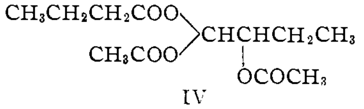
Oxidation of *n*-butyl *n*-butyrate led to the production of a new compound, 1-acetoxy-1-butyroxybutane (II), and a second compound whose structure has not been definitely established. This latter compound is undoubtedly a secondary oxidation product resulting from the acetoxylation of II. The two most likely structures for this product are III and IV. Structure III can be eliminated, however, because hydrolysis of the unknown compound yields only three moles of acid. Consequently, judging by saponification equivalent and C-H analysis, structure IV is most likely to be correct.



II



III



IV

Whereas *n*-propyl acetate reacted smoothly to give the expected product, propylidene diacetate, the oxidation of methyl acetate proved to be quite difficult under the conditions employed. The primary product, methylene diacetate, was isolated only in very small amounts. This undesirable result is most probably caused by (a) the limit placed upon the reflux temperature of the solution by the low-boiling ester, (b) the fact that attack must take place at an unreactive primary carbon atom, and (c) the greater relative reactivity toward lead tetraacetate of the reaction products (especially methylene diacetate) in comparison with methyl acetate itself.

gem-Diesters[6] such as methylene diacetate and propylidene diacetate are readily prepared by mineral acid-catalyzed reaction of acetic anhydride on formaldehyde and propionaldehyde, respectively. A significant result of the present reaction, however, is that when the starting compound is an ester of an acid other than acetic acid (*cf. n*-butyl *n*-butyrate, above) the product obtained is necessarily a mixed diester of a *gem*-diol. There could be found in the literature only one reference to compounds of this type; in 1884, Rubencamp[7] described the synthesis of 1-acetoxy-1-butyroxyethane (and several other compounds of analogous structure) by the action of silver butyrate on (α-chloroethyl) acetate.

In view of the above experiments, it is believed that the absence of methyl acetate in Kharasch's[3] oxidation of acetic acid could possibly have been caused by interaction of the ester with the oxidizing agent. In order to prove that methyl acetate is indeed a product of the oxidation of acetic acid, a deliberate attempt was made to isolate the methyl acetate by sweeping it from the reaction mixture before it had an opportunity to react with the lead tetraacetate. This method served to yield 1.3% methyl acetate, and it thereby places acetic acid in the same category as the higher homologs[2] of the acid series with regard to behavior toward lead tetraacetate.

In the light of the previously proposed mechanism[2] of decomposition of tetravalent lead salts of organic acids, the course of the ester oxidations can be readily explained. The mechanism proposed will be exemplified here by consideration of the case of *n*-butyl *n*-butyrate.

Criegee[8] has employed the formulation Pb-$(OAc)_3^{\oplus}$ which is essentially equal to our $CH_3CO\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{}^+$ Professor Criegee's structure would have a greater stability than ours and is probably a more accurate representation of the intermediate.

Reaction 5 will proceed in the absence of more reactive compounds as shown by Kharasch's[3] study of the decomposition of lead tetraacetate in acetic acid. In the presence of an ester, however, reaction 4 predominates because ion V is more stable than ion VI. Indeed, no acetoxyacetic acid could be isolated from the ester oxidation mixture. In order for solvent ion VI to stablize itself by resonance, an actual positive charge must mo-

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[3] For a complete study of this reaction, see M. S. Kharasch, H. N Friedlander and W. J. Urry, *J. Org. Chem.*, **16**, 533 (1951).

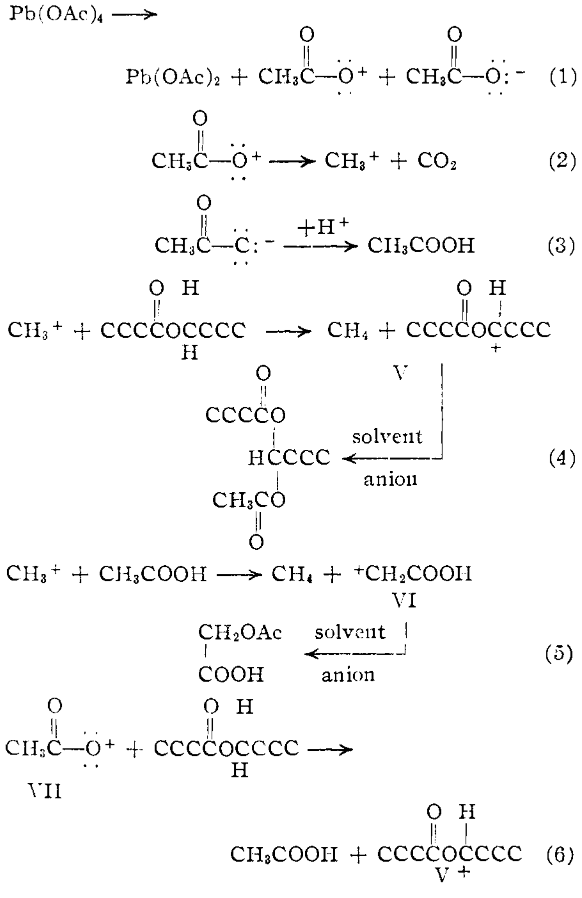
[4] Attempts to prepare I have been reported by R. Wegscheider and E. Späth, *Monatsh.*, **30**, 845 (1909). W. Spring, *Ber.*, **14**, 759 (1881), found acetic anhydride and acetone as product of the reaction of silver acetate with 2,2-dichloropropane.

[5] This compound itself is attacked by lead tetraacetate; see O. Dimroth and R. Schweizer, *Ber.*, **56B**, 1375 (1923).

[6] R. Wegscheider and E. Späth, *Monatsh.*, **30**, 841, 845 (1909).

[7] R. Rubencamp, *Ann.*, **225**, 267 (1884).

[8] R. Criegee, *Angew. Chem.*, **70**, 173 (1958).



$$Pb(OAc)_4 \longrightarrow Pb(OAc)_2 + CH_3\overset{O}{\overset{\|}{C}}-\ddot{\underset{..}{O}}{}^{+} + CH_3\overset{O}{\overset{\|}{C}}-\ddot{\underset{..}{O}}{:}^{-} \quad (1)$$

$$CH_3\overset{O}{\overset{\|}{C}}-\ddot{\underset{..}{O}}{}^{+} \longrightarrow CH_3^{+} + CO_2 \quad (2)$$

$$CH_3\overset{O}{\overset{\|}{C}}-\ddot{\underset{..}{C}}{:}^{-} \xrightarrow{+H^{+}} CH_3COOH \quad (3)$$

$$CH_3^{+} + CCCC\overset{O}{\overset{\|}{C}}O\overset{H}{\underset{H}{C}}CCC \longrightarrow CH_4 + CCCC\overset{O}{\overset{\|}{C}}O\overset{H}{\overset{|}{\underset{+}{C}}}CCC$$

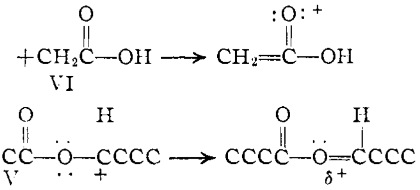
$$\text{V} \xrightarrow{\text{solvent anion}} \begin{array}{c} CCCC\overset{O}{\overset{\|}{C}}O \\ | \\ HCCCC \\ | \\ CH_3\underset{O}{\underset{\|}{C}}O \end{array} \quad (4)$$

$$CH_3^{+} + CH_3COOH \longrightarrow CH_4 + \underset{\text{VI}}{{}^{+}CH_2COOH}$$

$$\xrightarrow{\text{solvent anion}} \begin{array}{c} CH_2OAc \\ | \\ COOH \end{array} \quad (5)$$

$$\underset{\text{VII}}{CH_3\overset{O}{\overset{\|}{C}}-\ddot{\underset{..}{O}}{}^{+}} + CCCC\overset{O}{\overset{\|}{C}}O\overset{H}{\underset{H}{C}}CCC \longrightarrow CH_3COOH + CCCC\overset{O}{\overset{\|}{C}}O\overset{H}{\overset{|}{\underset{\text{V}\,+}{C}}}CCC \quad (6)$$

mentarily reside on the carboxyl oxygen atom (see electronic formula diagram below). In carbonium ion V, on the other hand, the alcoholic oxygen can participate in the stabilization simply by donating one of its extra electron pairs



$$\underset{\text{VI}}{{}^{+}CH_2\overset{O}{\overset{\|}{C}}-OH} \longrightarrow CH_2{=}\overset{:O:^{+}}{\overset{\|}{C}}-OH$$

$$\underset{\text{V}}{CCCC\overset{O}{\overset{\|}{C}}-\ddot{\underset{..}{O}}-\overset{H}{\underset{+}{C}}CCC} \longrightarrow CCCC\overset{O}{\overset{\|}{C}}-\ddot{O}{=}\overset{H}{\overset{|}{\underset{\delta+}{C}}}CCC$$

In ions of type V, hyperconjugation structures are also possible contributors to the stability of the ion.

A further reaction which must be considered in order to explain fully the mechanism of decomposition of lead tetraacetate is shown by reaction 6. It has been noted that the molar quantities[9] of carbon dioxide and methane obtained in any one reaction presumably *via* reaction 2 are generally of the same order of magnitude; in each case, however, the amount of carbon dioxide (and methane) corresponds only to about 20–70% of the theoretical value of one mole per mole of lead tetraacetate. Furthermore, the molar amount of acetic acid obtained in various reactions[10] in which this value could be obtained (resulting presumably from reaction 3 above) has been observed to amount to as high as 41% more than the theoretical value of one mole per mole of lead tetraacetate. It appears, therefore, that a significant part of the oxidizing power of lead tetraacetate is derived from a source other than the methyl carbonium ion. Ion VII is presumably capable of this function and can, consequently, be considered somewhat similar to the methyl carbonium ion in terms of stability, reactivity and method of attack on hydride ion donors.

A further argument in favor of the methyl carbonium ion intermediate proposed above is the complete dissimilarity of the reaction path in comparison with the established action of the methyl free radical on esters reported by Kharasch[11a,b] and co-workers. They found that the methyl radical (from decomposition of diacetyl peroxide) invariably abstracts a hydrogen atom from the α-carbon atom of the acidic component of the ester; the organic radical thus formed dimerizes in excellent yield to give the corresponding diester of a dicarboxylic acid. Radicals such as $\cdot CH_2COOH$ (in contrast to the corresponding carbonium ion VI) are apparently very stable because there is no necessity for establishing a positively charged oxygen atom in the resonance isomers.

Experimental

Oxidation of *n*-Propyl Acetate.—A solution of 200 ml. of glacial acetic acid and 66.5 g. (0.65 mole, b.r. 101.0–101.5°) of *n*-propyl acetate was treated with lead tetraacetate (126.5 g., 0.285 mole) and heated to reflux (119°). After 12 hours at this temperature, reaction was complete and the solution turned from yellow-green to brown. The cooled reaction mixture was added to 2.5 liters of rapidly stirred anhydrous ether. The ether solution was filtered and distilled through a Whitmore–Lux column (20 plate) packed with Podbielniak Heli-pak packing. Propylidene diacetate[12] (11.4 g., 25%) distilled at 73–78°(11 mm.), $n^{20}{}_{D}$ 1.4083. *Anal.* Calcd. for $C_7H_{14}O_4$: C, 52.49; H, 7.55; sapon. equiv., 80.08. Found: C, 51.56; H, 7.92; sapon. Equiv., 78.1. When boiled with water for one hour, the diester hydrolyzed to give propionaldehyde (2,4-dinitrophenylhydrazone m.p. and mixed m.p. 155–156°). The Ascarite tubes provided at the exit end of the condenser had absorbed 6.71 g. (53.5%) of CO_2. Copious amounts of an inflammable gas (presumably methane[13]) were evolved during the reaction, but the amount was not measured. The lead salts of the reaction were re-dissolved in glacial acetic acid and saturated with dry HCl gas (ice cooling). After filtering the lead chloride, the filtrate was distilled. No further products, such as acetoxyacetic acid, were found, however.

Oxidation of Isopropyl Acetate.—The lead tetraacetate (114.5 g., 0.26 mole), isopropyl acetate (61.2 g., 0.6 mole,

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(9) The only experiment in which the volume of methane was measured in the present communication is the oxidation of methyl acetate, in which the CO_2:CH_4 ratio in terms of % yield is 69:51. M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.*, **16**, 533 (1951), however, report a CO_2:CH_4 ratio of 42:30 in the decomposition of lead tetraacetate in acetic acid and a ratio of 16:16 in the decomposition of lead tetraacetate in diisopropyl ether.

(10) It is practicable to measure the amount of acetic acid formed from lead tetraacetate in a reaction only in those cases when a solvent other than acetic acid is used. For example, Kharasch[9] reports 136% acetic acid in the decomposition of lead tetraacetate in diisopropyl ether. Likewise, W. A. Mosher and C. L. Kehr, THIS JOURNAL, **75**, 3172 (1953), report yields of 126 and 141% acetic acid resulting from the decomposition of lead tetraacetate in isovaleric acid and isobutyric acid, respectively.

(11) (a) M. S. Kharasch, E. V. Jensen and W. H. Urry, *J. Org. Chem.*, **10**, 386 (1945); (b) M. S. Kharasch, H. C. McBay and W. H. Urry, *ibid.*, **10**, 394 (1945).

(12) R. Wegscheider and E. Späth, *Monatsh.*, **30**, 845 (1909).

(13) The identification of methane as a major reaction product of lead tetraacetate decompositions has been previously established by other workers; see ref. 3 and L. W. Wright, Ph.D. Dissertation, University of Delaware, 1951.

b.p. 88–88.5°) and glacial acetic acid (200 ml.) were heated with stirring to the reflux temperature for 7 hours. At this time the yellow-green color of the solution had turned to a red-black and the reaction was complete. The Ascarite tubes at the exit end of the reflux condenser had absorbed 5.12 g. (44.7%) of CO_2; an inflammable gas (presumably methane[13]), was produced but the quantity not measured.

The black reaction mixture, when cool, was added slowly to 2.5 liters of rapidly stirred anhydrous ether. The ether solution was decanted from the sandy heavy mass of lead salts and eventually fractionated through a 20-plate Whitmore–Lux column after first stripping the ether through a 3-foot Vigreux column. The fraction b.p. 40–41° at 12.5 mm.(5.18 g., 19.5%) was acetic anhydride, $n^{20}D$ 1.3882. When boiled with aniline gave acetanilide, m.p. and mixed m.p. 112.5–114°. Inspection of the pot residue and the mass of lead salts failed to yield any further identifiable products.

Oxidation of *n*-Butyl-*n*-Butyrate.—The lead tetraacetate (199 g., 0.45 mole), glacial acetic acid (200 ml.) and *n*-butyl-*n*-butyrate (120 g., 0.83 mole, b.p. 165–165.5°) were mixed and heated at the reflux temperature (124–129°) for 11 hours until reaction was complete. The Ascarite had absorbed 8.73 g. (44.1%) of CO_2. Again an inflammable gas (presumably methane[13]) was evolved. Two products were obtained by distillation: (1) 1-acetoxy-1-butyoxybutane, b.p. 95–97° (4.5 mm.), $n^{20}D$ 1.4210. *Anal.* Calcd. for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97; sapon. equiv., 101.1. Found: C, 58.76; H, 8.55; sapon. equiv., 98.9. Prolonged boiling with water yielded *n*-butyraldehyde, 2,4-dinitrophenylhydrazone m.p. and mixed m.p. 121–122°. (2) B.p. 138–140° (4 mm.), 7.48 g., 12.8%. *Anal.* Calcd. for $C_{12}H_{20}O_6$: C, 55.37; H, 7.73; sapon. equiv., 86.76. Found: C, 56.10; H, 7.79; sapon. equiv., 87.24. Attempts to prepare a derivative of the hydrolysis product failed. This substance is probably 1-acetoxy-1-butyroxy-2-acetoxybutane rather than the expected 1,1-diacetoxy-1-butyroxybutane (saponification equivalent 65.07).

Investigation of the pot residues and the lead salts failed to yield any other identifiable products.

Oxidation of Methyl Acetate.—The reaction flask in this run was fitted with a Dry Ice cooled reflux condenser. The gaseous reaction products were passed through a series of Ascarite tubes into a receiver designed to collect methane[13] by water displacement. Meticulously dried lead tetraacetate (200 g., 0.45 mole) was suspended in 200 ml. of glacial acetic acid (dried over Na_2SO_4) and the mixture heated to the reflux temperature (125°). Then freshly distilled methyl acetate (40 g., 0.54 mole) was added slowly over a period of 12 hours, whereupon the reflux temperature dropped gradually to 110°. After 35 hours at constant reflux, the lead tetraacetate was completely consumed. The Ascarite had absorbed 17.5 g. (69.7%) of CO_2 and a total of 6,550 ml. (51.3%) of inflammable gas (presumably methane[13]) was collected. Upon distillation (as described above) the only product which could be isolated was methylene diacetate (1.92 g., 2.6%), b.p. 55–60° at 10 mm.[14] This was hydrolyzed by boiling with $CaCO_3$ solution to formaldehyde (dimedon derivative m.p. and mixed m.p. 189–190°. The lead salts and pot residues were studied, but no further products could be obtained.

Methyl Acetate from Oxidation of Acetic Acid.—The reaction flask was fitted with an inefficient air-cooled reflux condenser for this experiment. To the outlet of the condenser was attached a series of three Ascarite-filled U-tubes, a Dry Ice cooled trap and a bubble counter.

Lead tetraacetate (217 g., 0.49 mole) was suspended in 520 ml. of glacial acetic acid and heated to the reflux temperature (116–122°). At the same time a moderately rapid stream of N_2 was passed through the reaction mixture to aid in sweeping out low-boiling products. After 26 hours, the solution turned from yellow to black and reaction was complete. The Dry Ice trap contained 0.46 g. (1.3) of methyl acetate, $n^{20}D$ 1.3599. This was derivatized by reaction with anilinomagnesium bromide (Hardy[15]) to obtain acetanilide, m.p. and mixed m.p. 113–114°.

The amount of CO_2 produced was not determined. The function of the Ascarite tubes in this case was simply to absorb the acetic acid vapors swept over by the flow of N_2 gas and permit the methyl acetate to come into the Dry Ice trap in the pure state.

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[14] I. Heilbron, "Dictionary of Organic Compounds," Oxford Univ. Press, 1953, Vol. 3, p. 371.

[15] D. V. N. Hardy, *J. Chem. Soc.*, 398 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANS.]

The Reactions of Recoil Tritium Atoms with Unsaturated Acids

BY R. MILFORD WHITE AND F. S. ROWLAND[1]

RECEIVED FEBRUARY 16, 1960

Recoil tritium atoms substitute into all of the hydrogen positions of crystalline *cis*- and *trans*-cinnamic acid and of sodium *trans*-cinnamate. The specific activities of the different positions of the aromatic ring are within 25% of each other for the *trans* compounds (and benzoic acid), and decrease in the oder *ortho* > *para* > *meta*. The specific activity of the *o*-position in *cis*-cinnamic acid is about half that of the *m*- and *p*-positions, perhaps because of steric interference by the -COOH group. Replacement of non-labile hydrogen by recoil tritium in maleic and fumaric acids is accompanied by geometric *cis–trans* isomerization in less than 5% of the substitutions. Addition to the double bond to form succinic acid is about half as frequent as substitution for hydrogen in the parent molecule. Addition to the triple bond of phenylpropiolic acid leads to labeled cinnamic acid, more than 90% in the *trans* form. The substitution of tritium for hydrogen is explained in terms of high kinetic energy reactions involving a miniumum of atomic motion during substitution.

Introduction

Previous studies of $Li^6(n,\alpha)T$ recoil reactions have shown that energetic tritium atoms are able to substitute for H atoms in many organic compounds.[2] Intramolecular degradations, when performed, have shown that the tritium atoms are not uniformly substituted throughout the molecule, but are found in varying specific activities in all of the non-labile hydrogen positions.[3-6] The crystalline molecules thus far investigated have been too complex for interpretation of the variations; heavily irradiated samples have also shown different distributions in separate irradiations. The present work has been undertaken in order to determine the influence of certain

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[1] The results presented in this paper are taken from a thesis presented by R. Milford White to the Universty of Kansas in partial fulfillment of the requirements for the Ph.D. degree. This work was supported by Contract No. At-(11-1)-407 with the United States Atomic Energy Commission.

[2] F. S. Rowland and R. Wolfgang, *Nucleonics*, **14**, No. 8, 58 (1956).

[3] F. S. Rowland, C. N. Turton and R. Wolfgang, THIS JOURNAL, **78**, 2358 (1956).

[4] H. Keller and F. S. Rowland, *J. Phys. Chem.*, **62**, 1373 (1958).

[5] W. J. Hoff, Jr., and F. S. Rowland, THIS JOURNAL, **79**, 4867 (1957).

[6] W. G. Brown and J. L. Garnett, *Intl. J. Appl. Rad. and Isotopes*, **5**, 114 (1959).