deuterated products were recorded in deuteriochloroform. Since benzylaniline, *meso*-1,2-dianilino-1,2-diphenylethane, and *dl*-1,2-dianilino-1,2-diphenylethane each have two benzylic hydrogens, the areas of the respective nmr peaks served to measure the composition of the reduction products. Examination of a known authentic mixture suggested that the results given in Table I are accurate to within ±2%. Furthermore, only nmr signals characteristic of the above-mentioned reduction products or of residual benzalaniline or its hydrolysis products were observed. Specifically, no bibenzyl signals were observed in any of the nmr spectra (possible product from reductive rupture of C–N bonds in the dimers).

Reduction of Benzalaniline by Means of the 1:1 Lithium–Biphenyl Adduct.—The blue-green solution of the 1:1 lithium–biphenyl adduct was prepared by stirring 0.52 g (0.075 g-atom) of lithium pieces with 11.58 g (0.075 mole) of biphenyl in 100 ml of THF. After 10 hr at room temperature, there was almost no trace of undissolved lithium. To this solution was added in one portion 0.05 g (0.005 mole) of benzalaniline dissolved in 50 ml of THF. The reaction mixture was stirred at room temperature for 96 hr during which time the mixture gradually became brownish red. After a terminal reflux period of 1 hr, the solution was cooled and hydrolyzed. Ethyl ether was added to enhance the volume of the organic extract. The separated ether layer was dried over anhydrous calcium sulfate and the solvent was thereupon removed by vacuum evaporation. The organic layer was dissolved in 150 ml of benzene and the resulting solution was saturated with gaseous hydrogen chloride. The precipitated amine hydrochlorides were collected on a glass frit and the filtrate was resaturated with gaseous hydrogen chloride. This treatment was repeated until no more solid was obtained. The solid hydrochloride mixture was warmed with a 10% solution of sodium hydroxide in aqueous ethanol (75%). By dilution of the cooled mixture with water the mixture of amines was obtained. An nmr analysis was carried out in the aforementioned manner.

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Reactions of Triphenyltin Hydride with Certain Acid Chlorides and Carboxylic Acids

EUGENE J. KUPCHIK AND ROBERT J. KIESEL

Department of Chemistry, St. John's University, Jamaica, New York 11432

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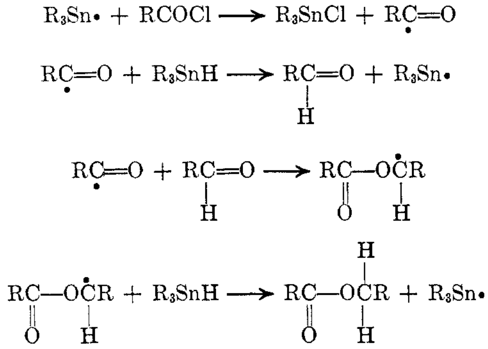
With the exception of triptoyl chloride and ferrocenoyl chloride, the principal reduction product of the reaction of certain aliphatic, bridgehead, and aromatic acid chlorides with triphenyltin hydride is the corresponding ester; a minor reduction product (less than 16%) is the corresponding aldehyde. Triptoyl chloride gives mostly aldehyde, while ferrocenoyl chloride gives ferrocenecarboxylic anhydride. Triphenyltin hydride reacts with bridgehead carboxylic acids and pyrrole-2-carboxylic acid to give the corresponding triphenyltin esters, whereas with ferrocenecarboxylic acid it gives either the triphenyltin ester or *sym*-tetraphenyldiferrocenoyloxyditin; with pyridine-2-carboxylic acid it gives diphenyltin dipicolinate. Thirteen new compounds, including eight new tin esters, are described.

It has been reported[1] that the reduction of benzoyl chloride with tri-*n*-butyltin hydride in ether gives benzaldehyde (54%) as the major reduction product; in the absence of solvent, benzyl benzoate (58%) predominates. Some evidence suggesting the following radical mechanism has been presented.[1]



$$R_3Sn\cdot + RCOCl \longrightarrow R_3SnCl + R\underset{\bullet}{C}{=}O \quad (1)$$

$$R\underset{\bullet}{C}{=}O + R_3SnH \longrightarrow R\underset{\underset{H}{|}}{C}{=}O + R_3Sn\cdot \quad (2)$$

$$R\underset{\bullet}{C}{=}O + R\underset{\underset{H}{|}}{C}{=}O \longrightarrow R\underset{\underset{O}{\|}}{C}{-}O\overset{\bullet}{\underset{\underset{H}{|}}{C}}R \quad (3)$$

$$R\underset{\underset{O}{\|}}{C}{-}O\overset{\bullet}{\underset{\underset{H}{|}}{C}}R + R_3SnH \longrightarrow R\underset{\underset{O}{\|}}{C}{-}O\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}R + R_3Sn\cdot \quad (4)$$

It has been reported[2] also that benzaldehyde, identified as the 2,4-dinitrophenylhydrazone, and triphenyltin chloride are formed when benzoyl chloride is heated with triphenyltin hydride (I). In contrast, we found[3] that reaction of benzoyl chloride with I in refluxing diethyl ether or benzene, or without solvent at the ambient temperature, gives benzyl benzoate as the major reduction product; in none of our runs could benzaldehyde be detected. The reaction was retarded by radical inhibitors and accelerated by azobisisobutyronitrile, a result which is consistent with the radical mechanism shown above.

Our results with benzoyl chloride led us to investigate the reactions of I with certain other acid chlorides. The results are summarized in Table I. With the exception of triptoyl chloride and ferrocenoyl chloride, the principal reduction product was the ester; a minor reduction product (less than 16%) was the aldehyde. In contrast with the results reported for tri-*n*-butyltin hydride,[1] use of a solvent did not significantly increase the yield of aldehyde. It is interesting to note that 2-thenoyl chloride resembled benzoyl chloride[3] in its behavior since only a very small amount of aldehyde was formed. Triptoyl chloride gave a relatively high yield of aldehyde. In this case steric factors may prevent the occurrence of reaction 3. Ferrocenoyl chloride unexpectedly gave ferrocenecarboxylic anhydride. How the anhydride was formed in this case remains to be ascertained. It had been prepared previously by the reaction of pyridine and traces of water with ferrocenoyl chloride.[4] Its formation was also observed, instead of the expected peroxide, in the reaction of ferrocenoyl chloride and sodium peroxide.[5]

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[1] H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 81 (1964).

[2] G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.* (London), **7**, 356 (1957).

[3] E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 3690 (1964).

[4] E. M. Acton and R. M. Silverstein, *ibid.*, **24**, 1487 (1959).

[5] H. H. Lau and H. Hart, *ibid.*, **24**, 280 (1959).

TABLE I

REACTIONS OF TRIPHENYLTIN HYDRIDE (I) WITH ACID CHLORIDES

			% yield		
Expt	Acid chloride	Conditions[a]	Ester[b]	Aldehyde[c]	Triphenyltin chloride[b]
1	Propionyl	Neat, ambient	*d*	14.0	62.6
2	Propionyl	Neat, ambient	50.0	*d*	90.0
3	Propionyl	Diethyl ether, reflux	*d*	15.4	*d*
4	Phenylacetyl	Neat, ambient	90.0	*d*	82.9
5	Phenylacetyl	Neat, ambient	*d*	6.6	*d*
6	Phenylacetyl	Diethyl ether, reflux	*d*	12.5	*d*
7	1-Apocamphanecarbonyl	Neat, ambient	*d*	15.0	*d*
8	1-Apocamphanecarbonyl	Neat, ambient	*d*	*d*	80.5[e]
9	1-Apocamphanecarbonyl	Neat, ambient	76.6	7.5, 8.0[b]	83.1
10	1-Apocamphanecarbonyl	Diethyl ether, reflux	*d*	13.2	*d*
11	1-Norbornanecarbonyl	Neat, ambient	*d*	11.1	*d*
12	1-Norbornanecarbonyl	Neat, ambient	80.1	*d*	83.1
13	Triptoyl	Benzene, reflux	*d*	61.9	80.4
14	2-Thenoyl[f]	Neat, 80°	*d*	*d*	70.2[g]
15	2-Thenoyl	Benzene, reflux	28.8[h]	*d*	70.0
16	2-Thenoyl	Benzene, reflux	*d*	1.2	*d*
17	Ferrocenoyl	Neat, ice–water temp, 3 hr	0[i]	*d*	83.0

[a] All reactions were carried out for 24 hr except for expt 17. [b] The yields are based on product isolation. [c] Unless otherwise noted, the yields are based on the 2,4-dinitrophenylhydrazone derivative. [d] Not determined. [e] In another run, a yield of 74.6% was obtained. [f] When the conditions were neat, ambient, 48 hr, 2-thenoyl chloride (85%) was recovered. When the conditions were diethyl ether, reflux, 48 hr, 2-thenoyl chloride (77%) and triphenyltin hydride (79%) were recovered. [g] When the conditions were benzene at reflux, the yield was 61.4%. [h] In two other runs, the yields were 30.1 and 27.7%. [i] Ferrocenecarboxylic anhydride (54.5%) was obtained. In another run, ferrocenecarboxylic anhydride (70.4%) and triphenyltin chloride (58.4%) were obtained.

TABLE II

REACTIONS OF TRIPHENYLTIN HYDRIDE (I) WITH CARBOXYLIC ACIDS

Expt	Carboxylic acid	Moles of hydride / mole of carboxylic acid	Product (% yield)
1	1-Apocamphanecarboxylic	1	Triphenyltin apocamphane-1-carboxylate (78.3)
2	1-Apocamphanecarboxylic	2	Triphenyltin apocamphane-1-carboxylate (80.2)
3	1-Norbornanecarboxylic	1	Triphenyltin norbornane-1-carboxylate (77.7)
4	1-Triptycenecarboxylic (triptoic)	1	Triphenyltin triptoate (84.3)
5	1-Triptycenecarboxylic (triptoic)	2	Triphenyltin triptoate (88.1)
6	Pyrrole-2-carboxylic	1	Triphenyltin pyrrole-2-carboxylate (38.0)
7	Pyrrole-2-carboxylic	2	Triphenyltin pyrrole-2-carboxylate (46.6)
8	Pyridine-2-carboxylic (picolinic)	2	Diphenyltin dipicolinate (90.9)
9	Ferrocenecarboxylic	1	Triphenyltin ferrocenoate (27.6)
10	Ferrocenecarboxylic	2	*sym*-Tetraphenyldiferrocenoyloxyditin (58.0)

The ferrocenoyl chloride used in the present study was prepared by allowing ferrocenecarboxylic acid to react, for the first time, with phosphorus trichloride. Previously, phosphorus pentachloride had been used.[6] Ferrocenecarboxylic anhydride was prepared by allowing ferrocenoyl chloride to react, for the first time, with sodium ferrocenoate. A new ferrocene ester, ferrocenoyloxymethylferrocene, was prepared by allowing ferrocenoyl chloride to react with hydroxymethylferrocene.

We also investigated the reactions of I with certain carboxylic acids. The results are summarized in Table II. The bridgehead carboxylic acids behaved like aliphatic carboxylic acids[7] in that only the corresponding triphenyltin esters were obtained. Ferrocenecarboxylic acid behaved somewhat like 2-thenoic and 2-furoic acids[7]; the corresponding triphenyltin ester was obtained when the molar ratio of I:acid was 1:1, while *sym*-tetraphenyldiferrocenoyloxyditin was obtained when the molar ratio of I:acid was 2:1. Pyrrole-2-carboxylic acid, on the other hand, gave the triphenyltin ester when the molar ratio of I:acid was 1:1 or 2:1. Pyridine-2-carboxylic acid unexpectedly gave diphenyltin dipicolinate when the molar ratio of I:acid was 2:1. How the diester was formed in this case remains to be ascertained.

The triphenyltin esters in Table II were also obtained by allowing the appropriate sodium carboxylate to react with triphenyltin chloride or bromide, and also by allowing the appropriate carboxylic acid to react with the triphenyltin bromide–benzylamine complex. *sym*-Tetraphenyldiferrocenoyloxyditin was further obtained by the method of Sawyer and Kuivila,[8] which involved allowing ferrocenecarboxylic acid to react with diphenyltin dihydride. An attempt to prepare *sym*-tetraphenyldipicolinoyloxyditin by this method gave, instead, a high yield of diphenyltin dipicolinate.

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[6] See K. Plesske, *Angew. Chem. Intern. Ed. Engl.*, **1**, 322 (1962), for pertinent references.

[7] S. Weber and E. I. Becker, *J. Org. Chem.*, **27**, 1258 (1962).

[8] A. K. Sawyer and H. G. Kuivila, *ibid.*, **27**, 610 (1962).

Diphenyltin dipicolinate was obtained unexpectedly from the reaction of sodium picolinate with triphenyltin bromide (1:1 molar ratio) also. It was further obtained, as expected, from the reaction of sodium picolinate with diphenyltin dichloride (2:1 molar ratio).

It was found that triphenyltin ferrocenoate is converted to diphenyltin diferrocenoate in high yield on passage through silica gel. This diester was also obtained from the reaction of triphenyltin ferrocenoate with ferrocenecarboxylic acid and also from the reaction of sodium ferrocenoate with diphenyltin dichloride (2:1 molar ratio).

To obtain further proof of structure, we wished to hydrolyze some of our triphenyltin esters. It was found that hydrolysis could be accomplished easily by chromatographing the ester on Woelm neutral alumina (activity II–III). Elution of the column first with petroleum ether (bp 30–60°) and then with methylene chloride served to remove the bis(triphenyltin) oxide. The carboxylic acid was then removed as its ammonium salt by elution with 10% aqueous ammonium hydroxide. In a typical run, triphenyltin ferrocenoate gave bis(triphenyltin) oxide (70.0%) and ferrocenecarboxylic acid (86.9%).

Carbonyl absorption as in organic esters[9] at approximately 1735 cm^{-1} was absent from all of our tin esters in the solid state and in solution, with the exception of diphenyltin dipicolinate. This absence of absorption is presumably due to coordination between carbonyl oxygen and tin and is in general agreement with published spectra in the solid state for trialkyltin carboxylates,[10] dialkyltin dicarboxylates,[11] and alkyltin tricarboxylates[12]; *sym*-tetraphenyldiaroyloxyditins have also been reported[7] to show no carbonyl absorption in the infrared as solids or in solution. In the case of diphenyltin dipicolinate, coordination between nitrogen and tin may be more significant than that between carbonyl oxygen and tin.

Considerable information concerning the mechanism of the reaction of diorganotin dihydrides with organic acids to give either diorganotin dicarboxylates or *sym*-tetraorganodiacyloxyditins has been obtained by Sawyer and Kuivila.[13] On the other hand, how *sym*-tetraorganodiaroyloxyditins are formed when ferrocenecarboxylic, benzoic,[7] 2-thenoic,[7] and 2-furoic acids[7] are treated with triphenyltin hydride remains to be ascertained.

Experimental Section

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. Each triphenyltin hydride reaction was carried out in an atmosphere of prepurified nitrogen. The aldehyde 2,4-dinitrophenylhydrazone, triphenyltin chloride, and ester obtained in each reaction were identified by mixture melting point determination (except for the liquid esters) and infrared spectral comparison with known samples. Elemental analyses and Rast molecular weight determinations were performed by Dr. G. Weiler and Dr. F. Strauss, Microanalytical Laboratory, Oxford, England. Tin analyses and thermoelectric[14] molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. The infrared data reported in microns were obtained with a Perkin-Elmer Infracord infrared spectrophotometer. The infrared data reported in reciprocal centimeters was obtained with a Perkin-Elmer Model 21 double-beam infrared spectrophotometer.

Propionyl Chloride and Triphenyltin Hydride. Expt 2.—The hard crystalline mass which remained after propionyl chloride (8.3 g, 0.09 mole) and I (31.6 g, 0.09 mole) had been allowed to react was slurried with 50 ml of petroleum ether (bp 30–60°) and filtered to give, after recrystallization from 95% ethanol, 31.2 g (90.0%) of triphenyltin chloride, mp 104–106°.

Evaporation of the petroleum ether left an oil, which on distillation gave 5.2 g (50.0%) of propyl propionate, bp 116–118° (lit.[15] bp 122°).

Expt 3.—After I (10.5 g, 0.03 mole) and propionyl chloride (2.77 g, 0.03 mole) had been allowed to react in 15 ml of diethyl ether, 50 ml of 95% ethanol and an excess of 2,4-dinitrophenylhydrazine reagent were added to give, after recrystallization first from 95% ethanol and then from cyclohexane, 1.1 g (15.4%) of propionaldehyde 2,4-dinitrophenylhydrazone, mp 146–148° (lit.[16] mp 154°).

Phenylacetyl Chloride and Triphenyltin Hydride. Expt 4.—The white crystalline mass which remained after I (17.5 g, 0.05 mole) and phenylacetyl chloride (7.7 g, 0.05 mole) had been allowed to react was slurried with 40 ml of petroleum ether and filtered to give 16.0 g (82.9%) of triphenyltin chloride, mp 103–105°.

Removal of the petroleum ether *in vacuo* and distillation of the residue gave 5.6 g (90.0%) of β-phenylethyl phenylacetate, bp 135–137° (0.05 mm) [lit.[17] bp 177–178° (4–5 mm)].

Expt 6.—The mixture remaining after I (7.0 g, 0.02 mole) and phenylacetyl chloride (3.1 g, 0.02 mole) had been allowed to react in 15 ml of diethyl ether was dissolved in 60 ml of 95% ethanol, and an excess of 2,4-dinitrophenylhydrazine reagent was added to give, after recrystallization from 95% ethanol–methylene chloride, 0.75 g (12.5%) of phenylacetaldehyde 2,4-dinitrophenylhydrazone, mp 234–236° (lit.[18] mp 240°).

1-Apocamphanecarbonyl Chloride and Triphenyltin Hydride. Expt 9.—The mixture remaining after 1-apocamphanecarbonyl chloride[19] (3.7 g, 0.02 mole) and I (7.0 g, 0.02 mole) had been allowed to react was sublimed at 120–130° (1 mm). The sublimate, which was collected in a flask cooled by a Dry Ice–acetone bath, was 1-apocamphanecarboxaldehyde, 0.24 g (8.0%), mp 182–184° (lit.[20] mp 187–189°); a mixture melting point with an authentic sample was undepressed. Addition of 10 ml of 95% ethanol followed by an excess of 2,4-dinitrophenylhydrazine reagent gave 0.5 g (7.5%) of 1-apocamphanecarboxaldehyde 2,4-dinitrophenylhydrazone, mp 201–203° (lit.[19] mp 201–202°).

Addition of 40 ml of petroleum ether to the residue from the sublimation, followed by filtration gave 6.4 g (83.1%) of triphenyltin chloride, mp 103–105°.

The filtrate was poured onto 25 g of Woelm neutral alumina (activity II–III), and the column was eluted with 500 ml of petroleum ether. Removal of the petroleum ether left a solid which afforded, after recrystallization from 95% ethanol, 2.3 g (76.6%) of (1-apocamphyl)methyl apocamphane-1-carboxylate, mp 132–134°.

(1-Apocamphyl)methyl Apocamphane-1-carboxylate.—The mixture obtained after 1-hydroxymethylapocamphane[19] (2.5 g, 0.016 mole) in 10 ml of dry pyridine was added to 1-apocamphanecarbonyl chloride[19] (3.36 g, 0.018 mole) was allowed to stand at room temperature overnight and then was poured into 500 ml of water containing 10 ml of concentrated ammonium hydroxide

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[9] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 44.

[10] R. Okawara, D. E. Webster, and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 3287 (1960).

[11] M. J. Janssen, J. G. A. Luijten, and G. J. M. van der Kerk, *Rec. Trav. Chim.*, **82**, 90 (1963).

[12] H. H. Anderson, *Inorg. Chem.*, **3**, 912 (1964).

[13] A. K. Sawyer and H. G. Kuivila, *J. Org. Chem.*, **27**, 837 (1962).

[14] Performed at 37° by the method of C. Tomlinson, *Mikrochim. Acta*, **3**, 457 (1961).

[15] "Dictionary of Organic Compounds," Vol IV, I. Heilbron and H. M. Bunbury, Ed., Oxford University Press, New York, N. Y., 1953, p 238.

[16] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 320.

[17] H. Hibbert and C. P. Burt, *J. Am. Chem. Soc.*, **47**, 2242 (1925).

[18] Reference 15, p 95.

[19] M. Sprecher, M. Feldkimel, and M. Wilchek, *J. Org. Chem.*, **26**, 3664 (1961).

[20] W. v. E. Doering, M. Farber, M. Sprecher, and K. B. Wiberg, *J. Am. Chem. Soc.*, **74**, 3000 (1952).

solution. The solid material which formed was collected on a filter and recrystallized from 95% ethanol to give 3.8 g (78.2%) of (1-apocamphyl)methyl apocamphane-1-carboxylate, mp 130–132°, λ_{max}^{KBr} 5.8 (COO) μ.

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.89; H, 10.60. Found: C, 78.59; H, 10.66.

1-Norbornanecarbonyl Chloride and Triphenyltin Hydride. Expt 11.—The semisolid mixture which remained after I (3.51 g, 0.01 mole) and 1-norbornanecarbonyl chloride[21] (1.58 g, 0.01 mole) had been allowed to react was dissolved in 20 ml of 95% ethanol, and an excess of 2,4-dinitrophenylhydrazine reagent was added to give 0.35 g (11.1%) of 1-norbornanecarboxaldehyde 2,4-dinitrophenylhydrazone, mp 172–174°. Recrystallization from acetonitrile raised the melting point to 187–189° (lit.[21] mp 190–191°).

Expt 12.—The mixture which remained after I (3.51 g, 0.01 mole) and 1-norbornanecarbonyl chloride (1.58 g, 0.01 mole) had been allowed to react was slurried with 30 ml of petroleum ether and filtered to give 3.2 g (83.1%) of triphenyltin chloride, mp 103–105°.

The filtrate was poured onto 50 g of Fisher neutral alumina, and the column was eluted with 1000 ml of petroleum ether. Removal of the petroleum ether from the eluate *in vacuo*, followed by distillation of the residue, gave 1.0 g (80.1%) of (1-norbornyl)-methyl norbornane-1-carboxylate, bp 103° (0.05 mm), mp 77–79°.

(1-Norbornyl)methyl Norbornane-1-carboxylate.—1-Norbornanecarbonyl chloride[21] (0.47 g, 0.003 mole) was added in small portions to an ice-cold solution of 1-hydroxymethylnorbornane[21] (0.30 g, 0.0024 mole) in 10 ml of anhydrous pyridine. The mixture was allowed to stand at room temperature overnight and then was poured into 200 ml of water containing 5 ml of concentrated ammonium hydroxide. The solid which separated was collected on a filter, dried, and distilled to give 0.476 g (80.1%) of (1-norbornyl)methyl norbornane-1-carboxylate, bp 102–103° (0.05 mm), mp 77–79°, λ_{max}^{KBr} 5.78 (COO) μ.

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.16; H, 9.71.

Triptoyl Chloride and Triphenyltin Hydride. Expt 13.—After triptoyl chloride[22] (3.16 g, 0.01 mole) and I (3.51 g, 0.01 mole) were allowed to react in 10 ml of refluxing benzene, the benzene was removed *in vacuo*. The residue was extracted twice with 50-ml portions of 95% ethanol, and the extracts were concentrated to 20 ml. Addition of an excess of 2,4-dinitrophenylhydrazine reagent gave 2.8 g (61.9%) of triptaldehyde 2,4-dinitrophenylhydrazone, mp 224–226° dec.

Anal. Calcd for $C_{27}H_{18}N_4O_4$: C, 70.12; H, 3.92; N, 12.11. Found: C, 69.98; H, 4.18; N, 11.88.

The ethanol mother liquor was diluted with 500 ml of water, causing the precipitation of a solid which gave, after recrystallization from 95% ethanol, 3.1 g (80.4%) of triphenyltin chloride, mp 102–104°.

2-Thenoyl Chloride and Triphenyltin Hydride. Expt 15.—After I (28.0 g, 0.08 mole) and 2-thenoyl chloride[23] (11.6 g, 0.08 mole) were allowed to react in 30 ml of refluxing benzene, the benzene was evaporated with a stream of nitrogen, and the residue was slurried in 50 ml of petroleum ether and filtered to give 20.5 g (66.5%) of triphenyltin chloride, mp 104–106°.

The filtrate was poured onto 70 g of Woelm neutral alumina (activity grade II–III), and the column was eluted with 400 ml of petroleum ether. Removal of the petroleum ether from the eluate, followed by distillation of the residue (oil), gave 2.6 g (28.8%) of 2-thenyl-2-thenoate, bp 125–132° (0.04 mm), mp 30–32°.

Further eluation of the column with 700 ml of petroleum ether, followed by evaporation of the petroleum ether from the eluate, gave an additional 2.3 g of triphenyltin chloride, mp 103–105° (total yield, 70.0%).

Expt 16.—After 2-thenoyl chloride (2.93 g, 0.02 mole) and I (7.0 g, 0.02 mole) were allowed to react in 20 ml of refluxing benzene, the benzene was evaporated with a stream of nitrogen, and the residue was dissolved in 30 ml of 95% ethanol. The solid which precipitated (after several hours) on addition of 2,4-dinitrophenylhydrazine reagent was collected on a filter and recrystallized from ethanol–methylene chloride to give 0.14 g (1.19%) of 2-thiophenecarboxaldehyde 2,4-dinitrophenylhydrazone, mp 230–232° (lit.[24] mp 233–236°).

2-Thenyl 2-Thenoate.—2-Thenoyl chloride[23] (8.94 g, 0.055 mole) was added in small portions to an ice-cold solution of 2-thenyl alcohol (5.70 g, 0.05 mole) in 20 ml of pyridine. The mixture was allowed to stand at room temperature overnight and then was poured into 400 ml of ice–water containing 20 ml of concentrated ammonium hydroxide solution. The oil that separated was extracted with diethyl ether, and the diethyl ether extract was washed with water and dried over anhydrous magnesium sulfate. The diethyl ether was removed *in vacuo*, and the residue was distilled to give 9.0 g (80.3%) of 2-thenyl 2-thenoate, bp 121–123° (0.05 mm), mp 31–32°, λ_{max}^{film} 5.84 (COO) μ.

Anal. Calcd for $C_{10}H_8O_2S_2$: C, 53.54; H, 3.59; S, 28.59. Found: C, 53.52; H, 3.35; S, 27.85.

Ferrocenoyl Chloride.—Ferrocenecarboxylic acid (3.5 g, 0.015 mole), phosphorus trichloride (0.67 g, 0.005 mole), and benzene (150 ml) were refluxed under a nitrogen atmosphere for 1.5 hr. The mixture was cooled, and the benzene was decanted from the insoluble oil (phosphorous acid) and evaporated *in vacuo*. The residue was recrystallized from *n*-hexane to give 3.2 g (86.3%) of ferrocenoyl chloride as red crystals, mp 47–49° (lit.[5] mp 49°); other yields obtained were 81.0, 82.0, and 80.7%.

Concentrated aqueous ammonia converted the chloride to the amide, mp 168–170° after recrystallization from chloroform–petroleum ether (lit.[5] mp 167–168°).

Ferrocenoyl Chloride and Triphenyltin Hydride. Expt 17.—The hard red crystalline mass obtained from the reaction of I (3.51 g, 0.01 mole) and freshly prepared ferrocenoyl chloride (2.48 g, 0.01 mole) was dissolved in 40 ml of warm 95% ethanol to give, on cooling, 1.7 g of dark red needles, mp 110–113°. Recrystallization from cyclohexane–methylene chloride gave 1.2 g (54.5%) of ferrocenecarboxylic anhydride, mp 125–128° (lit.[5] mp 141–142°). Recrystallization from ethyl acetate raised the melting point to 139–140°; a mixture melting point with a sample prepared as described below was undepressed.

The ethanol mother liquor was evaporated to dryness, and the residue was slurried with 25 ml of petroleum ether and poured onto 50 g of Woelm neutral alumina (activity II–III). Elution of the column with 1000 ml of petroleum ether, followed by removal of the petroleum ether from the eluate, left 4.2 g of solid, which was slurried with petroleum ether and filtered, giving 3.2 g (83.0%) of triphenyltin chloride, mp 101–103°.

Ferrocenecarboxylic Anhydride.—Ferrocenoyl chloride (2.48 g, 0.01 mole), sodium ferrocenoate (2.52 g, 0.01 mole), and 50 ml of dry chloroform were refluxed for 24 hr, the insoluble material was filtered, and the chloroform was evaporated from the filtrate *in vacuo*, leaving 3.6 g of red solid, mp 125–128°. Recrystallization from heptane–methylene chloride gave 2.6 g (60.0%) of ferrocenecarboxylic anhydride, mp 139–141° (lit.[5] mp 141–142°), λ_{max}^{KBr} 5.64 and 5.83 (COOCO) μ.

Anal. Calcd for $C_{22}H_{18}Fe_2O_3$: C, 59.78; H, 4.08. Found: C, 59.77; H, 4.30.

Ferrocenoyloxymethylferrocene.—Ferrocenoyl chloride (1.49 g, 0.006 mole) was added in small portions to an ice-cold solution of hydroxymethylferrocene (1.08 g, 0.005 mole), prepared as described below, in 20 ml of pyridine. The mixture was allowed to stand at room temperature overnight and then was poured into 200 ml of ice-cold water. The granular precipitate was collected on a filter and recrystallized from ethyl acetate–petroleum ether to give 1.6 g (74.8%) of ferrocenoyloxymethylferrocene, mp 176–178°, λ_{max}^{KBr} 5.87 (COO) μ.

Anal. Calcd for $C_{22}H_{20}Fe_2O_2$: C, 61.75; H, 4.68. Found: C, 61.98; H, 4.90.

Hydroxymethylferrocene was prepared by the lithium aluminum hydride reduction of ferrocenecarboxylic acid. From 2.3 g (0.01 mole) of ferrocenecarboxylic acid there was obtained, after recrystallization from *n*-hexane, 2.0 g (93.0%) of hydroxymethylferrocene, mp 76–78° (lit.[25] mp 81–82°).

1-Apocamphanecarboxylic Acid and Triphenyltin Hydride. Expt 1.—A solution of 1-apocamphanecarboxylic acid (3.36 g, 0.02 mole) and I (7.0 g, 0.02 mole) in 20 ml of *n*-heptane was refluxed for 20 hr, the solvent was removed by distillation *in vacuo*, and the residue was extracted with 50 ml of warm diethyl ether. Removal of the diethyl ether left a white crystalline

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solid (9.4 g), mp 80–83°, which, after recrystallization from ethyl acetate–petroleum ether, afforded 8.1 g (78.3%) of triphenyltin apocamphane-1-carboxylate: mp 91–92°, no depression on admixture with samples obtained by methods A and B below; $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1621 (COO) cm^{-1}; $\bar{\nu}_{\max}^{\mathrm{CCl_4}}$ 1621 (COO) cm^{-1}.

Anal. Calcd for $C_{28}H_{30}O_2Sn$: C, 65.01; H, 5.85; Sn, 22.95; mol wt, 517.2. Found: C, 64.98; H, 5.76; Sn, 23.07; mol wt, 419 (Rast), 645 (dibromomethane).

Triphenyltin Apocamphane-1-carboxylate. A.—A mixture of sodium apocamphane-1-carboxylate (2.5 g, 0.013 mole), triphenyltin bromide (5.6 g, 0.013 mole), and 95% ethanol (100 ml) was refluxed for 22 hr, the solvent was removed by distillation, and the residue was extracted with two 50-ml portions of warm diethyl ether. Removal of the diethyl ether and recrystallization of the residue from ethyl acetate–petroleum ether gave 3.6 g (53.7%) of triphenyltin apocamphane-1-carboxylate, mp 90–91°.

B.—A solution of 1.25 g (0.0117 mole) of benzylamine in 100 ml of chloroform was added rapidly to a solution of 5.0 g (0.0117 mole) of triphenyltin bromide in 50 ml of chloroform, and the turbid solution was stirred at 25° for 2 hr. A solution of 1.96 g (0.0117 mole) of 1-apocamphanecarboxylic acid in 50 ml of chloroform was added, and the white solid formed was collected on a filter to give 1.9 g (86.1%) of benzylammonium bromide, mp 221–223°, no depression on admixture with an authentic sample.

Evaporation of the chloroform from the filtrate, followed by recrystallization of the residue from ethyl acetate–petroleum ether, afforded 4.9 g (80.1%) of triphenyltin apocamphane-1-carboxylate, mp 90–91°.

1-Norbornanecarboxylic Acid and Triphenyltin Hydride. Expt 3.—A solution of 1-norbornanecarboxylic acid (1.4 g, 0.01 mole) and I (3.51 g, 0.01 mole) in 20 ml of *n*-heptane was refluxed for 20 hr, the solvent was removed *in vacuo*, and the residue was extracted with 50 ml of diethyl ether. Evaporation of the ether left an oil, which was dissolved in 10 ml of petroleum ether and allowed to stand at 0° overnight. The solid which separated was collected on a filter (4.1 g, mp 75–77°) and recrystallized from ethanol to give 3.8 g (77.7%) of triphenyltin norbornane-1-carboxylate, mp 80–82°, no depression on admixture with the sample prepared as described below: $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1631 (COO) cm^{-1}; $\bar{\nu}_{\max}^{\mathrm{CCl_4}}$ 1631 (COO) cm^{-1}.

Anal. Calcd for $C_{26}H_{26}O_2Sn$: C, 63.84; H, 5.36; Sn, 24.26; mol wt, 489.16. Found: C, 63.65; H, 5.51; Sn, 23.85; mol wt, 460 (Rast), 617 (dibromomethane).

Triphenyltin Norbornane-1-carboxylate.—Following the procedure for the preparation of triphenyltin apocamphane-1-carboxylate, from 1.40 g (0.01 mole) of 1-norbornanecarboxylic acid there was obtained 3.6 g (73.6%) of triphenyltin norbornane-1-carboxylate, mp 80–82°.

1-Triptycenecarboxylic Acid and Triphenyltin Hydride. Expt 4.—A mixture of 1-triptycenecarboxylic acid (2.98 g, 0.01 mole), I (3.51 g, 0.01 mole), and *n*-heptane (25 ml) was refluxed for 24 hr, and the mixture was filtered to give 6.0 g of solid, mp 210–212°. Recrystallization from benzene–methylene chloride gave 5.5 g (84.3%) of triphenyltin triptoate: mp 215–217°, no depression on admixture with a sample prepared as described below; $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1629 (COO) cm^{-1}.

Anal. Calcd for $C_{39}H_{28}O_2Sn$: C, 72.36; H, 4.36; mol wt, 647.3. Found: C, 72.20; H, 4.45; mol wt, 674 (benzene).

Triphenyltin Triptoate.—Following the procedure used for the preparation of triphenyltin apocamphane-1-carboxylate, from 2.98 g (0.01 mole) of 1-triptycenecarboxylic acid there was obtained 5.1 g (78.8%) of triphenyltin triptoate, mp 213–215°.

Pyrrole-2-carboxylic Acid and Triphenyltin Hydride. Expt 6.—A mixture of pyrrole-2-carboxylic acid (2.22 g, 0.02 mole), I (7.0 g, 0.02 mole), and *n*-heptane (25 ml) was refluxed for 24 hr, the solvent was removed *in vacuo*, and the residue was extracted with 40 ml of hot ethanol, leaving 1.8 g of insoluble material which did not melt below 360° and was not identified.

The ethanol extract on standing deposited 4.0 g of solid, mp 137–140°, which afforded, after recrystallization from 95% ethanol, 3.5 g (38.0%) of triphenyltin pyrrole-2-carboxylate: mp 141–143°, no depression on admixture with a sample prepared as described below; $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1603 (COO) cm^{-1}.

Anal. Calcd for $C_{23}H_{19}NO_2Sn$: C, 60.05; H, 4.16; N, 3.04; mol wt, 460.09. Found: C, 60.11; H, 4.44; N, 3.20; mol wt, 550 (benzene).

Triphenyltin Pyrrole-2-carboxylate.—Following the procedure used for the preparation of triphenyltin apocamphane-1-carboxylate, from 2.22 g (0.02 mole) of pyrrole-2-carboxylic acid there was obtained 6.0 g (63.0%) of triphenyltin pyrrole-2-carboxylate, mp 143–145°.

Picolinic Acid and Triphenyltin Hydride. Expt 8.—A mixture of picolinic acid (2.46 g, 0.02 mole), I (14.0 g, 0.04 mole), and *n*-heptane (25 ml) was refluxed for 24 hr, and the mixture was filtered to give 5.1 g of solid, mp 274–275°, which afforded, after recrystallization from chloroform, 4.7 g (90.9%) of diphenyltin dipicolinate: mp 281–283°, no depression on admixture with samples prepared by methods A, B, and C below; $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1681, 1605 (COO) cm^{-1}.

Anal. Calcd for $C_{24}H_{18}N_2O_4Sn$: C, 55.76; H, 3.50; N, 5.41; Sn, 22.95; mol wt, 517.1. Found: C, 55.52; H, 3.52; N, 5.28; Sn, 22.95; mol wt, 541 (benzene).

Diphenyltin Dipicolinate. A.—Diphenyltin dichloride (13.7 g, 0.04 mole) was reduced with excess lithium aluminum hydride in diethyl ether,[8] and the ether solution, after drying over calcium chloride, was treated with picolinic acid (3.69 g, 0.03 mole) for 24 hr. The ether-insoluble material was collected on a filter (8.0 g, mp 275–279°) and recrystallized from ethyl acetate–methylene chloride to give 7.4 g (95.3%) of diphenyltin dipicolinate, mp 281–283°.

B.—A mixture of triphenyltin bromide (12.9 g, 0.03 mole), sodium picolinate (4.35 g, 0.03 mole), and 95% ethanol (150 ml) was refluxed for 24 hr, cooled, and then filtered to give 5.2 g (67.5%) of diphenyltin dipicolinate, mp 280–282°.

C.—A mixture of diphenyltin dichloride (3.44 g, 0.01 mole), sodium picolinate (2.90 g, 0.02 mole), and 95% ethanol (75 ml) was refluxed for 24 hr, cooled, and filtered to give 4.8 g of solid, mp 265–268°, which afforded, after recrystallization from benzene–chloroform, 4.4 g (85.1%) of diphenyltin dipicolinate, mp 280–282°.

Ferrocenecarboxylic Acid and Triphenyltin Hydride. Expt 9.—A mixture of ferrocenecarboxylic acid (2.30 g, 0.01 mole), I (3.51 g, 0.01 mole), and *n*-heptane (20 ml) was refluxed for 24 hr, cooled, and filtered to give 1.3 g of unreacted ferrocenecarboxylic acid. The *n*-heptane was removed from the filtrate *in vacuo*, the residue was dissolved in 25 ml of petroleum ether, and the solution was cooled at 0° overnight. The solid which was present was collected on a filter (2.1 g, mp 117–119°) and recrystallized from ethyl acetate–petroleum ether to give 1.6 g (27.6%) of triphenyltin ferrocenoate: mp 121–123°, no depression on admixture with samples prepared by methods A and B below; $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1608 (COO) cm^{-1}; $\bar{\nu}_{\max}^{\mathrm{CCl_4}}$ 1621 (COO) cm^{-1}.

Anal. Calcd for : $C_{29}H_{23}FeO_2Sn$: C, 60.26; H, 4.01; mol wt, 578.0. Found: C, 60.15; H, 4.14; mol wt, 760 (benzene).

Expt 10.—A mixture of ferrocenecarboxylic acid (2.30 g, 0.01 mole), I (7.0 g, 0.02 mole), and *n*-heptane (25 ml) was refluxed for 24 hr, the solvent was removed by distillation *in vacuo*, and the residue was extracted with 50 ml of warm benzene. Concentration of the benzene extract, followed by filtration, gave 2.0 g of *sym*-tetraphenyldiferrocenoyloxyditin, mp 180–182°; a second crop of 0.9 g was obtained, mp 178–180°, giving a total yield of 58.0%: a mixture melting point with a sample prepared as described below was undepressed; $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1506, 1475 (COO) cm^{-1}.

Anal. Calcd for $C_{46}H_{36}Fe_2O_4Sn_2$: C, 55.15; H, 3.62; Sn, 23.70; mol wt, 1001.8. Found: 54.80; H, 3.56; Sn, 23.59; mol wt, 1147 (benzene).

Triphenyltin Ferrocenoate. A.—Following the procedure used for the preparation of triphenyltin apocamphane-1-carboxylate, from 2.79 g (0.0117 mole) of ferrocenecarboxylic acid there was obtained 5.6 g of solid, mp 113–115°, which afforded, after recrystallization from ethyl acetate, 4.2 g (62.1%) of triphenyltin ferrocenoate, mp 122–124°.

B.—A mixture of sodium ferrocenoate (2.5 g, 0.01 mole), triphenyltin chloride (3.86 g, 0.01 mole), and 95% ethanol (75 ml) was refluxed for 24 hr, the solvent was removed *in vacuo*, and the residue was extracted twice with 50-ml portions of hot petroleum ether. The petroleum ether was concentrated to 25 ml, cooled at 0° overnight, and filtered to give 3.5 g of bronze-colored crystals, mp 116–118°, which afforded, after recrystallization from ethyl acetate, 2.9 g (50.2%) of triphenyltin ferrocenoate, mp 121–123°.

***sym*-Tetraphenyldiferrocenoyloxyditin.**—Diphenyltin dichloride (6.87 g, 0.02 mole) was reduced with excess lithium aluminum hydride in diethyl ether.[8] The ether solution, after drying over calcium chloride, was treated with ferrocenecarboxylic acid (4.6 g, 0.02 mole) for 24 hr, the solvent was removed *in* *vacuo*, and the residue was extracted with 40 ml of warm benzene. There remained 1.1 g of unreacted ferrocenecarboxylic acid. Cooling of the benzene extract at 0° for several hours gave 4.0 g (40.0%) of *sym*-tetraphenyldiferrocenoyloxyditin as bronze-colored crystals, mp 180–182°. Recrystallization from ethyl acetate did not raise the melting point.

Diphenyltin Diferrocenoate. A.—Triphenyltin ferrocenoate, mp 120–122° (0.587 g, 0.001 mole), was slurried with 40 ml of petroleum ether and poured onto 40 g of silica gel. The column was eluted with 500 ml of petroleum ether, which, on evaporation, gave a small amount (*ca.* 0.1 g) of unchanged triphenyltin ferrocenoate, mp 120–122°. Further elution with 1000 ml of methylene chloride gave, after evaporation, 0.46 g of solid, which, after recrystallization from benzene–petroleum ether, afforded 0.34 g of diphenyltin diferrocenoate: mp 240–241°, no depression on admixture with samples prepared by methods B and C below; $\tilde{\nu}_{\max}^{\mathrm{KBr}}$ 1517, 1486, 1471 (COO) cm^{-1}.

Anal. Calcd for $C_{34}H_{28}Fe_2O_4Sn$: C, 55.86; H, 3.86. Found: C, 56.07; H, 3.81.

B.—A mixture of sodium ferrocenoate (1.26 g, 0.005 mole), diphenyltin dichloride (0.86 g, 0.0025 mole), and 95% ethanol (25 ml) was refluxed for 24 hr, the solvent was removed *in vacuo,* and the residue was extracted twice with 100-ml portions of benzene–methylene chloride (1:1). Concentration of the extract to 20 ml gave 0.55 g (30.2%) of diphenyltin diferrocenoate, mp 241–243°.

C.—A mixture of ferrocenecarboxylic acid (0.23 g, 0.001 mole), triphenyltin ferrocenoate (0.578 g, 0.001 mole), and 95% ethanol (10 ml) was refluxed for 24 hr, cooled, and filtered to give 0.6 g of orange solid, mp 236–238°. Recrystallization from benzene–methylene chloride gave 0.5 g (68.5%) of diphenyltin diferrocenoate, mp 241–243°.

Hydrolysis of Triphenyltin Esters on Woelm Alumina. A.—Triphenyltin ferrocenoate (0.578 g, 0.001 mole) was slurried with 40 ml of petroleum ether and poured onto 40 g of Woelm neutral alumina (activity II–III). The column was eluted first with 1000 ml of petroleum ether and then with 500 ml of methylene chloride. Evaporation of the methylene chloride *in vacuo* left 0.350 g of solid, which afforded, after recrystallization from 95% ethanol, 0.25 g (70.0%) of bis(triphenyltin) oxide, mp 119–121°. A mixture melting point with an authentic sample was undepressed. The infrared spectrum was superimposable on that of an authentic sample.

Further elution with 10% aqueous ammonium hydroxide gave 250 mg of solid, which was dissolved in water and acidified with concentrated hydrochloric acid to give, after filtration, 0.200 g (86.9%) of ferrocenecarboxylic acid, mp 218–222°, no depression on admixture with an authentic sample.

B.—Following the procedure described in A above, there was obtained from 1.0 g (0.0022 mole) of triphenyltin pyrrole-2-carboxylate, 0.5 g (70.0%) of bis(triphenyltin) oxide, and 0.17 g (70.0%) of pyrrole-2-carboxylic acid.

Mechanism of Ozonation Reactions. II. Aldehydes

Ronald E. Erickson,[1] Dennis Bakalik, Charles Richards, Michael Scanlon,
and George Huddleston

Department of Chemistry, Canisius College, Buffalo, New York 14208

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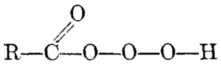
Aldehydes react with ozone by an electrophilic mechanism (ρ values -1.1 to -0.6) in ethyl acetate and in pyridine. The deuterium isotope effect on ozone-catalyzed autoxidation, a reaction involving radical abstraction of hydrogen, was $k_H/k_D = 7.8$ at 0°, while decreasing the amount of autoxidation by decreasing the amount of oxygen or selectively destroying peroxidic material with pyridine gave k_H/k_D values from 1.2 to 2.0. It is suggested that initial attack of ozone on aldehydes involves either the direct insertion of ozone into the carbon–hydrogen σ bond, as postulated by White and Bailey, or the formation of a five-membered ring which then rearranges to the same intermediate.

White and Bailey have recently reinvestigated the reaction of ozone with aldehydes.[2] Their work showed that, contrary to previous reports,[3] per acids are formed when aldehydes are ozonized with either ozone–oxygen or ozone–nitrogen streams. They also determined, by product analysis after 1 mole equiv. of ozone had been passed through three *para*-substituted benzaldehydes, the reactivity sequence *p*-MeO > *p*-H > *p*-NO$_2$ and concluded that initial attack of ozone on aldehydes is not nucleophilic. This fact, along with other information from their rather complete product analysis, led to the proposal of I as the initial product of ozonation. I might then decompose to give various radicals which would catalyze the autoxidation of the aldehyde.



$$R-C(=O)-O-O-O-H$$

I

Since Walling and McElhill[4] have shown the same reactivity sequence (*i.e.*, *p*-MeO > *p*-H > *p*-CN) for the free-radical catalyzed autoxidation of aldehydes, some caution must be exercised in interpreting Bailey's reactivity sequence.

Slomp and Johnson[5] have argued that the presence of pyridine in a solvent mixture greatly decreases the rate of the electrophilic addition of ozone to alkenes and have suggested that nucleophilic attack of ozone on aldehydes may take place when fairly large amounts of pyridine are present. They also note that, in the ozonation of alkenes, much less titratable peroxide is present when relatively small amounts of pyridine are present, while Bailey[6] reports the use of pyridine as a reducing agent for the decomposition of peroxides formed in the ozonation of pyrene. Supposedly, the product of these reductions is pyridine oxide, and Slomp gathered some evidence for its presence in his publication.[5]

We have been interested in the mechanism of the ozonation of aldehydes in particular and relative rates of ozonations in general for some time.[7] This paper reports our work on the relative rate method for the ozonation of various substituted benzaldehydes in ethyl acetate and in pyridine. The deuterium isotope effect k_H/k_D is also reported and discussed for benzalde-

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[1] To whom requests for reprints should be addressed: Chemistry Department, University of Montana, Missoula, Mont.

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