

If the preferential positions for migration of the allyl group are blocked, as with allyl 2,4,6-trichlorophenyl ether, cleavage of the allyl group is the major reaction upon treatment with diethylaluminum chloride, to form 2,4,6-trichlorophenol in 96% yield. However, substitution of benzene for hexane as the solvent causes the formation of 35% allylbenzene and 13% 1,2-diphenylpropane as well as a 94% yield of 2,4,6-trichlorophenol. Treatment of allylbenzene in benzene with diethylaluminum chloride results in formation of 1,2-diphenylpropane as the major product.

Other compounds such as 2-allyloxy-pyridine⁸ or allyl phenyl sulfide⁹ which are known to undergo the thermal Claisen rearrangement failed to rearrange when treated with diethylaluminum chloride at room temperature.

Experimental Section

The nmr spectra were obtained from a Varian HA-100 spectrometer with tetramethylsilane as internal standard. The infrared spectra were taken on a Perkin-Elmer Infracord. The gas chromatograph used for analyzing the composition of the off gases was F & M Model 5750, with a 5 ft \times 1/4 in. column containing a 80-100 mesh Porapak S support. The same instrument was used for analyzing the composition of allyl phenyl ether reaction mixture using a 6 ft \times 1/8 in. column containing 10% polyphenyl ether on 80-100 mesh Gas Chrom Q support. The allyl chlorophenyl ethers were analyzed with an F & M Model 720 using a 10 ft \times 1/4 in. column containing 28.6% Apiezon L on a 60-80 mesh Gas Chrom Z support. The product ratios obtained by glc were derived from the peak area ratios.

The following compounds were prepared according to the procedure of Tarbell and Wilson:¹⁰ allyl *o*-, *m*-, *p*-chlorophenyl ether; allyl 2,4-dichlorophenyl ether; allyl 2,6-dichlorophenyl ether; and allyl 2,4,5-trichlorophenyl ether. The following compounds were prepared by published procedures: allyl 2,4,6-trichlorophenyl ether;¹¹ 2-allyl-6-chlorophenol;¹² 2-allyloxy-pyridine;¹³ and allyl phenyl sulfide.⁹ Yields and physical properties were in good agreement with literature values.

Organoaluminum compounds used in this work were purchased from Texas Alkyls. Solvents were purified and dried by conventional methods and distilled prior to use. Reactions involving the organoaluminum reagents were carried out under dry nitrogen with the usual precautions for the rigorous exclusion of moisture and air.

General Procedure.—In a typical procedure, to a solution of 0.01 mol of allyl phenyl ether in 50 ml of hexane was added 0.02 mol of diethylaluminum chloride in hexane. After stirring for 30 min, the reaction mixture was hydrolyzed below 5° with dilute hydrochloric acid. The upper layer was separated and concentrated on a rotary evaporator.

Reaction of Allyl 2,4,6-Trichlorophenyl Ether with Diethylaluminum Chloride. A. In Hexane.—To 23.7 g (0.10 mol) of allyl 2,4,6-trichlorophenyl ether in 500 ml of hexane was added 0.15 mol of diethylaluminum chloride in hexane. After stirring for 3 hr, the reaction mixture was worked up below 5° by hydrolysis with dilute hydrochloric acid. The upper layer was separated and treated with a solution of 10 g of sodium hydroxide in 300 ml of water. The aqueous phase was acidified with dilute hydrochloric acid. The solids were filtered and air dried. There was obtained 18.9 g (95.8%) of 2,4,6-trichlorophenol melting at 65-66° (lit.¹¹ mp 67°).

B. In Benzene.—The reaction was carried out in the same manner using 400 ml of benzene, except that in the work-up 18.5 g (93.5%) of 2,4,6-trichlorophenol was isolated from the aqueous phase. On distillation of the organic phase through a short

fractionating column, there was obtained 4.1 g (34.8%) of liquid, bp 67-70° (20 mm), whose infrared spectrum was identical with that of allylbenzene, and 2.6 g (13.3%) of 1,2-diphenylpropane, bp 90-95° (0.5 mm), whose infrared spectrum was identical with that of an authentic sample, No. 2266 API Research Project 44.

Reaction of Allylbenzene with Diethylaluminum Chloride.—To a well-stirred solution of 11.9 g (0.10 mol) of allylbenzene in 300 ml of benzene was added 0.05 mol of diethylaluminum chloride in benzene. The mixture was kept at 60° for 30 min and stirred for an additional 30 min at room temperature. After hydrolysis below 10° with dilute hydrochloric acid, the upper layer was separated and concentrated on a rotary evaporator. Distillation gave 3.4 g (28.6%) of starting material, bp 60-62° (10 mm), and 3.9 g (39.8%) of 1,2-diphenylpropane, bp 121-125° (4 mm). *Anal.* Calcd for C₁₅H₁₆: C, 91.9; H, 8.1. Found: C, 92.0; H, 8.0. There remained behind 3.8 g of higher boiling material.

Registry No.—Allyl phenyl ether, 1746-13-0; diethylaluminum chloride, 96-10-6; ethylaluminum dichloride, 563-43-9; diisobutylaluminum chloride, 1779-25-5; allyl *o*-chlorophenyl ether, 20788-42-5; allyl *m*-chlorophenyl ether, 24824-86-0; allyl *p*-chlorophenyl ether, 13997-70-1; allyl 2,4-dichlorophenyl ether, 5441-16-7; allyl 2,4,5-trichlorophenyl ether, 16516-83-9; 2-allyloxy-pyridine, 5831-77-6; allyl phenyl sulfide, 5296-64-0; 1,2-diphenylpropane, 5814-85-7.

Oxidation of Carboxylic Acids and Anhydrides to Symmetrical Esters with Higher Valency Iodine

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Iodine in its higher valency forms can oxidize aliphatic acids or their anhydrides to symmetrical esters and carbon dioxide. The most efficient process involves the use of iodine triacylates and mercuric oxide and produces the corresponding esters in 70-90% yields for unbranched anhydrides. The synthesis is believed to involve a free-radical chain mechanism initiated by a homolytic thermolysis of an iodine-oxygen bond. Mercuric iodate and acid anhydrides also produce esters and, in the presence of olefins or ketones, produce olefinic or ketonic esters. Iodine triacylates are readily obtained by ozonation of solutions of iodine in aliphatic carboxylic acid anhydrides.

Recently, it was reported that tetravalent lead and iodine will oxidize carboxylic acids to symmetrical esters and carbon dioxide in substantial yields.⁴ The synthesis was shown to proceed in three separate steps, only the last of which was established and was shown to be a displacement reaction between lead(II) carboxylates and alkyl iodides. The present work was undertaken in an effort to determine the natures of the first two steps in the synthesis and if possible to develop a better synthesis for symmetrical esters.

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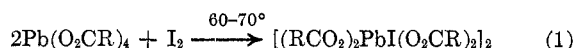
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(3) Commercial Solvents Corporation Research Assistant, 1966-1968.

(4) G. B. Bachman and J. W. Wittmann, *J. Org. Chem.*, **28**, 65 (1963).

A lead tetracarboxylate will decolorize 0.5 mol equiv of iodine at 60–70° without formation of ester or carbon dioxide, which accords with the following stoichiometry.

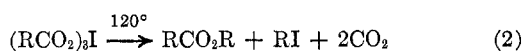


However, the reaction does not stop at this point, since after standing it was possible to isolate iodine triacylates, $(\text{RCO}_2)_3\text{I}$, from the mixture. Cooling the reaction mixture precipitated a white solid which was very sensitive to moisture and heat but which gave analyses for lead and iodine in a 1:1 atom ratio. Heating the mixture to 100° gave ester, alkyl iodide, carbon dioxide, and lead dicarboxylate in the ratios 1:2:3:2, respectively.

The above experiments suggested to us that the lead(IV) serves the purpose of oxidizing the iodine(0) to iodine(III), and the iodine(III), rather than the lead(IV), oxidizes the carboxyl group. This concept is in accord with the fact that lead(IV) carboxylates give very little ester when heated,⁵ while iodine triacylates, $(\text{RCO}_2)_3\text{I}$, give ester, alkyl iodide, and carbon dioxide in the ratio 1:1:2.⁶

Iodine can be converted to iodine(III) by oxidizing agents other than lead(IV). Of particular interest to us was the report of Beger⁷ that ozone reacts with iodine in acetic anhydride to yield a "solvated iodine trioxide complex" of the formula $3(\text{CH}_3\text{CO})_2 \cdot \text{I}_2\text{O}_3$. We have found that the reaction of ozone with iodine in carboxylic acid anhydrides provides an excellent general synthesis for the preparation of iodine triacylates. The composition of iodine triacetate differs only slightly from the composition of Beger's compound.

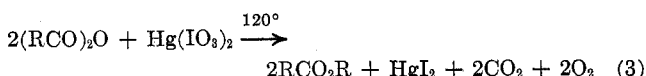
Thermal decomposition of iodine triacylates prepared by the above method follows the stoichiometry given by Oldham and Ubbelohde,⁶ which is shown in eq 2.



Thus 1.0 mol equiv of iodine ozonated in excess propionic anhydride and heated to 120° produced 1.54 mol equiv each of ethyl propionate and ethyl iodide (yields 77%) and 3.54 mol equiv of carbon dioxide (yield 88.5%).

In an attempt to prepare compounds of the complex type hypothesized in eq 1, various metal iodides were ozonated in acid anhydrides and the resulting mixtures heated to form ester and alkyl iodide. With the iodides of zinc, tin(IV), and lead(II) both ester and alkyl iodide were formed, but with mercury(II) iodide, only ester was formed, and mercuric iodide was regenerated quantitatively. In this case, analysis of the precipitate formed on ozonization showed it to be pure mercuric iodate.

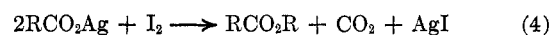
Commercially available mercuric iodate reacts with acid anhydrides according to the following equation.



Mercuric iodate (1 mol equiv) in excess propionic anhydride produced 1.88 mol equiv (94% yield) of ethyl propionate, while in excess octanoic anhydride it produced 0.92 mol equiv (46% yield) of heptyl octanoate and 0.60 mol equiv of heptane.

Since mercuric iodate alone does not evolve oxygen at temperatures below about 175°, it is probable that the anhydride produces an intermediate species which is less stable to oxygen elimination than is mercuric iodate itself.

A series of experiments demonstrated the unique ability of iodine among the halogens to generate esters. Thus mercuric bromate or chlorate gives no esters with acid anhydrides unless mercuric iodide or iodate is also present. This may correlate with the fact that iodine alone among the halogens exhibits a +3 oxidation state in which there are ten electrons in the outer shell of the iodine atom.⁸ On the other hand, iodine is not unique in its ability to oxidize carboxylic acids to alkyl halides. This is evident from the success of the Hunsdiecker reaction,⁹ the Kochi reaction,¹⁰ and the Cristol and Firth reaction¹¹ in the synthesis of alkyl halides. Simonini¹² has shown that the Hunsdiecker reaction may be adapted to the synthesis of esters if iodine is used



and we have shown that the Cristol and Firth reaction may also be adapted to the synthesis of esters if iodine and acid anhydride are used.

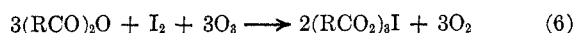


The yield of butyl valerate from valeric anhydride was 50% based upon iodine in the above equation.

It would appear that these two different types of decarboxylative oxidation reactions require two different oxidation states in the halogen atom, and that iodine alone is capable of generating esters.

Oxidation of acid anhydrides to esters with mercuric iodate suffers from certain disadvantages. In the first place, two-thirds of the available oxygen is lost as free oxygen, and in the second place the yields of ester decrease markedly among the higher anhydrides due to side oxidation reactions leading to the next lower aldehydes and acids. We have, therefore, developed a process of ester formation involving trivalent iodine for the decarboxylative oxidation and mercury for iodine scavenging.

When iodine dissolved in an acid anhydride (with or without added inert solvent) is ozonated, an equivalent amount of mercuric oxide added, and the mixture is heated to 120°, esters are formed in good yields even from the higher aliphatic acid anhydrides (Table I).



Branching at the α position sharply diminishes the yield of ester and the reaction fails with aromatic acid anhydrides. The high ratio of ester formed to mercury and iodine used (3:1) and the high yields of ester realized make this the method of choice for the synthesis of symmetrical esters among those studied.

Mechanistic Considerations.—Symmetrical ester formation in all of these processes is probably initiated by

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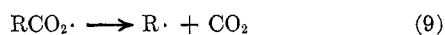
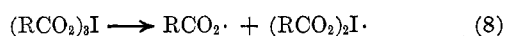
TABLE I
SYMMETRICAL ESTERS PRODUCED FROM THE REACTION OF ANHYDRIDES WITH
IODINE AND OZONE, FOLLOWED BY THERMAL DECOMPOSITION IN THE PRESENCE OF MERCURIC OXIDE

Anhydride ^a	CO ₂ , mol equiv	Ester, mol equiv	Yield, %
Propionic	2.68	Ethyl propionate, (2.56)	85.5
Valeric ^b	2.98	Butyl valerate, (2.28)	76
Caproic	2.94	Amyl caproate, (2.72)	91
Octanoic ^c	2.76	Heptyl octanoate, (2.20)	73.5
Stearic ^d		Heptadecyl stearate, (2.06)	69
2-Methylbutyric ^e	2.36	sec-Butyl 2-methylbutyrate, (0.52)	17.3
Pivalic	2.00	t-Butyl pivalate, (0.46)	15.4
Benzoic ^e		Phenyl benzoate	Trace ^e

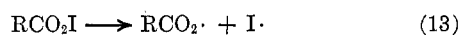
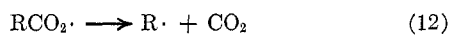
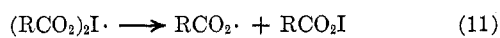
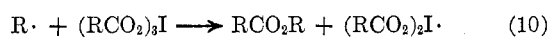
^a The anhydride was present in tenfold molar excess except where otherwise noted; 1.0 mol equiv of iodine was present in each case. ^b 1,1,2,2-Tetrachloroethane as solvent. ^c Anhydride present in eightfold molar excess. ^d 3.0 mol equiv of anhydride present; 1,2,3-trichloropropane as solvent. ^e Iodobenzene (46%) obtained; yield based on iodine.

homolytic thermolysis of an oxygen-iodine bond. The following series of reactions is in accord with the known facts.

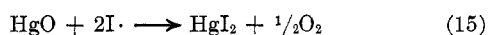
Initiation



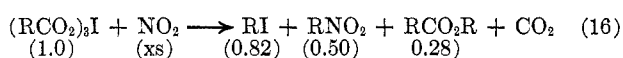
Propagation



Termination



In an attempt to capture the proposed alkyl radical intermediates, iodine tricaproate was decomposed in the presence of an excess of nitrogen dioxide.



The mole equivalents of reactants and products (in parentheses) indicate that the amyl radicals converted to 1-nitropentane are derived primarily from those yielding amyl caproate rather than those leading to amyl iodide formation, since the yield of ester is diminished more than that of the alkyl iodide.

Mercuric Iodate as an Oxidizing Agent.—In addition to its action on acid anhydrides alone, mercuric iodate reacts with active methylene groups in the presence of acid anhydrides to form acyloxy derivatives. Thus cyclohexanone, propionic anhydride, and mercuric iodate react to produce α -propionoxycyclohexanone and propionic acid. Reaction of cyclohexene, propionic anhydride, and mercuric iodate affords 2-cyclohexenyl propionate, and 1-octene yields two isomeric esters, *trans*-2-octenyl propionate, and 1-octen-3-yl propionate. The mixture of esters obtained in the latter reaction indicates the formation of an octenyl species free enough to isomerize before uniting with a propionoxy group to produce the observed esters.

Experimental Section

Apparatus.—A Welsbach Style T-23 Oxonator was employed as the source of ozonized oxygen (110 V, 6.0 psi O₂, flow rate 0.005–0.020 ft³/min).

Analysis by Glpc.—Throughout this work many of the conversions and yields reported were calculated from vpc analyses using the common thermal conductivity correction factor method. An Aerograph Model A-350-B dual column temperature gas chromatograph and an F & M Model 720 dual column temperature programmed gas chromatograph, fitted with the appropriate columns, were employed. Butyl valerate and heptyl octanoate were analyzed on a 6.0-ft 10% FFAP liquid phase on Chromosorb W DMCS A/W column. All other esters were analyzed on either a 6.0-ft or a 9.0-ft 10% diisodecyl phthalate liquid phase on Chromosorb W DMSC A/W column. Products were identified by comparison of gas chromatographic retention times and infrared and nuclear magnetic resonance spectra with those of authentic samples. Where necessary, mass spectral analyses were also obtained.

Materials.—All anhydrides employed were carefully distilled and exhibited not more than a 2° boiling point range. Mercuric iodate was obtained from the City Chemical Corporation of New York and dried over phosphorus pentoxide. This product gave poorer yields than ozonized mercuric iodide unless about 1% of iodine pentoxide was added to it.

Reaction of Lead Tetraacetate with Iodine.—Iodine (0.005 mol) was dissolved in warm (40–60°) trichloroethylene, lead tetraacetate (0.01 mol) was added with stirring, and the solution was allowed to stand overnight protected from atmospheric moisture. The white precipitate was separated by filtration and found to be extremely sensitive to moisture, turning brown in a few minutes when exposed to the air of the laboratory. Analyses showed an iodine:lead ratio of 1:1, but the results varied considerably with the details of preparation including the relative amounts of reactants and solvent. Heating of either the precipitate or the filtrate to 120° produced variable ratios of methyl acetate and methyl iodide. From a similar reaction of iodine and lead tetrastearate in carbon tetrachloride was isolated by concentration of the filtrate a small amount of iodine tristearate, mp 45–50°, CO₂ evolution at 100°, infrared absorption maxima at 7.25, 8.24, and 8.90 μ , similar constants to those reported previously.⁶

Preparation and Decomposition of Iodine Tripropionate.—In a flask equipped with a Dry Ice-acetone reflux condenser, an ozone inlet tube extending to the bottom of the flask, and a magnetic stirring bar, were placed 0.077 mol of propionic anhydride and 0.013 mol of iodine. Ozonized oxygen was passed through the stirred solution at 0°. The ozonation was deemed complete when the characteristic color of iodine had been discharged and replaced by yellow iodine tripropionate suspended in the solution. The ozone inlet tube was replaced by a ground-glass stopper. The small amount of yellow solid which adhered to the inlet tube turned dark brown and liberated iodine within 30 sec after exposure to the atmosphere. The Dry Ice-acetone reflux condenser was attached to a wet-test meter previously saturated with carbon dioxide. The stirred solution was then heated: a sudden and rather vigorous evolution of gas occurred at 120°. Gas evolution was completed within 5 min and a light wine-colored solution was obtained. Carbon dioxide, 0.046 mol (87.5% yield), was evolved. Vpc analysis revealed that 0.020 mol (77% yield) each of ethyl propionate and ethyl iodide were produced.

Ozonization of Metal Iodides in Acid Anhydrides and Thermal Decomposition of Products.—The metal iodide, 0.01 mol, was suspended in 20.0 g (excess) of the acid anhydride and ozonized with a 25% excess of the calculated amount of ozone. The re-

sulting mixture was heated at 120° under reflux until carbon dioxide evolution ceased, cooled, and filtered, and the filtrate was analyzed for ester and alkyl iodide. Using acetic anhydride, the following percentage yields were obtained per atom of iodine: ZnI₂, 16, 21; SnI₄, 87, 67; using butyric anhydride, PbI₂, 58, 24.

Mercuric iodide gave ester but very little or no alkyl iodide when employed in the above process. The precipitate formed upon ozonization of mercuric iodide in excess propionic anhydride was isolated by suction filtration, washed several times with carbon tetrachloride, and dried.

Anal. Calcd for Hg(IO₃)₂: Hg, 36.44; I, 46.12. Found: Hg, 36.28; I, 46.12.

Reaction of Propionic Anhydride with Mercuric Iodate.—In a flask equipped with a Dry Ice-acetone reflux condenser, a nitrogen inlet tube with a stopcock, and a magnetic stirring bar, were placed 0.050 mol of propionic anhydride and 0.0050 mol of mercuric iodate. A weighed Ascarite trap for carbon dioxide absorption was attached to the reflux condenser. A wet-test meter was attached to the Ascarite trap. Air was swept from the system by a stream of nitrogen. The stirred solution was heated until gas evolution ceased (0.0170 mol evolved), cooled to room temperature, and the wet-test meter was disconnected. The reaction flask was immersed in a Dry Ice-acetone bath, the nitrogen inlet tube stopcock was opened, and the residual gaseous product was swept through the Ascarite trap. Carbon dioxide, 0.0099 mol (99% yield), was found. The difference between total gas evolution, as measured by the wet-test meter, and carbon dioxide evolution, as measured by the Ascarite trap, was 0.0071 mol, a 72% yield of oxygen (identified by mass spectrometry). Quantitative vpc analysis of the liquid reaction mixture showed ethyl propionate, 0.0094 mol (yield 87% based on propionic anhydride), to be present. The reaction mixture was filtered and the filtrate was titrated to a phenolphthalein end point with standardized sodium hydroxide. Unreacted propionic anhydride, determined as propionic acid, 0.039 mol, was found. Air drying of the filtered solid yielded 0.0047 mol (94% yield) of mercuric iodide.

Reaction of Valeric Anhydride with Mercuric Oxide and Iodine.—In a flask equipped with a condenser, a pressure-equalizing dropping funnel, a thermometer, and a magnetic stirring bar, were placed 15 ml of 1,2-dibromoethane, 0.050 mol of valeric anhydride, and 0.050 mol of red mercuric oxide. A solution of 0.050 mol of iodine dissolved in 71 ml of 1,2-dibromoethane was placed in the dropping funnel. The slurry of valeric anhydride and mercuric oxide was heated with stirring, and the solution of iodine in 1,2-dibromoethane was slowly added. A temperature of 100° was required to decolorize the iodine. Gas evolution accompanied the decolorization. At the end of the iodine addition, gas evolution ceased and a clear solution containing red mercuric iodide was obtained. Vpc analysis revealed the presence of 0.025 mol of butyl valerate. Based upon iodine, the yield is 50%. Butyl iodide was not present.

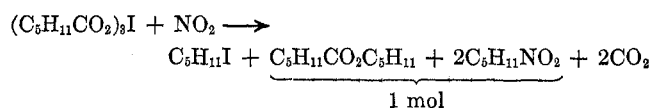
Decomposition of Iodine Tricaproate in the Presence of Mercuric Oxide.—A mixture of 0.025 mol of caproic anhydride and 0.0025 mol of iodine was ozonized, red mercuric oxide, 0.0026 mol, was added, and the stirred solution was heated. At 120° a sudden and vigorous evolution of gas occurred, accompanied by the appearance of free iodine throughout the solution. Within 60 sec, gas evolution ceased and the free iodine color disappeared. Yellow mercuric iodide soon precipitated from the colorless solution; upon cooling, the red crystalline modification was formed. Carbon dioxide, 0.0074 mol, was evolved. Vpc analysis revealed the presence of 0.0068 mol (91% yield) of amyl caproate.

The above procedure, with only minor modification, was employed for all the liquid anhydrides studied. In the case of the solid stearic anhydride, stoichiometric amounts of anhydride and iodine were employed in the solvent 1,2,3-trichloropropane, and the mercuric iodide was separated from the heptadecyl stearate by thorough washing with aqueous KI.

When mercuric oxide was replaced by lead(II) oxide in the above reaction, alkyl iodide but no ester was formed. With red lead (Pb₃O₄), both ester (36% yield) and alkyl iodide were obtained.

Decomposition of Iodine Tricaproate in the Presence of Excess Nitrogen Dioxide.—A suspension of iodine tricaproate in caproic anhydride was prepared as described immediately above. The ozone inlet tube was replaced with a nitrogen dioxide inlet tube, and excess nitrogen dioxide was passed into the solution. The solution was heated with stirring and maintained at 130–135° for

30 min. The solution was cooled to room temperature and analyzed by vpc. Amyl iodide, 0.0041 mol (82% yield), amyl caproate, 0.0014 mol (28% yield), and 1-nitropentane, 0.0050 mol (25% yield), were obtained. Yields are based on the following equation.



Reaction of Mercuric Iodate and Propionic Anhydride with Active Methylene Compounds.—A mixture of 0.010 mol each of propionic anhydride and cyclohexanone and 0.0035 mol of mercuric iodate was maintained at 135–140° under reflux for 12 hr. Upon cooling, a light wine-colored solution containing red mercuric iodide was obtained. Vpc analysis of the solution revealed ethyl propionate to be absent. The only major reaction products were α -propionoxycyclohexanone, 0.0022 mol (31% yield), and propionic acid.

Replacement of cyclohexanone with cyclohexene under the same reaction conditions afforded 0.0017 mol (24% yield) of 2-cyclohexenyl propionate and propionic acid as the only major reaction products.

Replacement of cyclohexanone with 1-octene produced 0.0015 mol (21% yield) of 1-octen-3-yl propionate, 0.0020 mol (29% yield) of *trans*-2-octenyl propionate, and propionic acid as the only major reaction products. These products were identified by ir, nmr, and mass spectra determined on samples isolated by vpc.

Registry No.—Ozone, 10028-15-6; propionic anhydride, 123-62-6; valeric anhydride, 2082-59-9; caproic anhydride, 2051-49-2; octanoic anhydride, 623-66-5; stearic anhydride, 638-08-4; 2-methylbutyric anhydride, 1519-23-9; pivalic anhydride, 1538-75-6; benzoic anhydride, 93-97-0; iodine tripropionate, 24824-83-7; mercuric iodate, 7783-32-6; mercuric oxide, 1344-45-2; iodine, 7553-56-2; iodine tricaproate, 24824-84-8.

Optically Active 1,2-Naphthalene Oxide

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Valence tautomerism in unsaturated medium ring systems is an area of considerable current interest.² Certain arene oxides (benzene oxide,³ 3,4-toluene oxide⁴) exist as equilibrium mixtures of oxide and oxepin forms, while others appear to exist solely in either the oxide (8,9-indan and 9,10-tetralin oxide)⁵ or the oxepin form (1,2-dimethyl-1,2-benzene oxide⁶). Spectroscopic studies on 1,2-naphthalene oxide (1) suggest that it exists solely in the oxide form but do not exclude the possibility of an equilibrium between 1 and 2 which greatly favors 1. If such an equilibrium does not exist or if it exists and the interconversion rate is slow, 1

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