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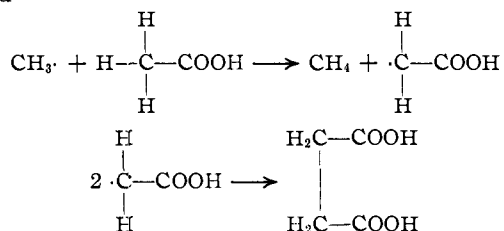
## Reactions of Atoms and Free Radicals in Solution. XII. The Addition of Bromo Esters to Olefins

BY M. S. KHARASCH, P. S. SKELL AND PAUL FISHER

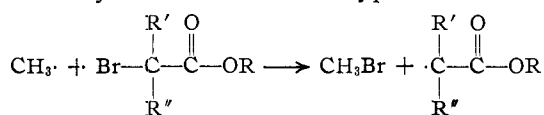
## Introduction

Investigation of the additions of a number of substances to olefins has demonstrated that some of these additions proceed by a free radical chain reaction. Among the reactions observed, are radical-induced polymerizations or copolymerizations, and additions of the following types of atoms and free radicals<sup>1</sup>: Br·,<sup>(a)</sup> RS·,<sup>(b)</sup> ·SCH<sub>2</sub>COOH,<sup>(c)</sup> HO<sub>2</sub>S·,<sup>(d)</sup> Cl<sub>3</sub>C·, Br<sub>3</sub>C·, Cl<sub>2</sub>BrC·, Br<sub>2</sub>HC·,<sup>(e)</sup> C<sub>2</sub>H<sub>5</sub>OCOCCL<sub>2</sub>·,<sup>(f)</sup> Cl<sub>2</sub>P·,<sup>(g)</sup> Cl<sub>3</sub>Si·,<sup>(h)</sup> (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C·.<sup>(k)</sup> The present paper deals with the free radical chain reactions involved in the additions of various bromo esters to olefins.

**Addition of Bromo Esters to Olefins.**—It has been shown that a free methyl radical, generated in solution by the thermal decomposition of diacetyl peroxide, abstracts an  $\alpha$ -hydrogen atom from carboxylic acids,<sup>2a</sup> esters, nitriles,<sup>2c</sup> ketones,<sup>2b</sup> etc. Where carboxylic acids are used, the products of the reaction<sup>2a</sup> are methane and a free carboxylic acid radical, which then dimerizes to the corresponding succinic or substituted succinic acid



The method cited for producing free carboxymethyl radicals or free carbalkoxymethyl radicals cannot, however, be used to study the reactions of these free radicals with olefins because olefins successfully compete with the acid or the ester for the free methyl radical. The same type of free carbalkoxymethyl radical is however produced when a free methyl radical acts on an  $\alpha$ -bromo ester.

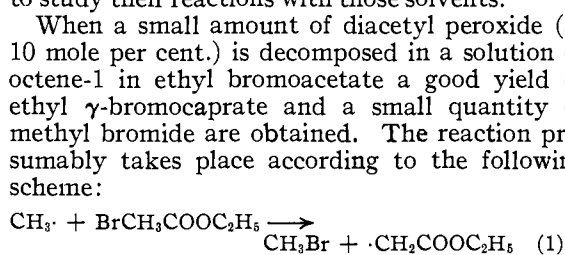


(1) (a) Kharasch, Englemann and Mayo, *J. Org. Chem.*, **2**, 288, 400, 577 (1937). (b) Kharasch and Mayo, *THIS JOURNAL*, **55**, 2491 (1933); Jones and Reid, *ibid.*, **60**, 2452 (1938); Kharasch, Nudenberg and Graham, unpublished work; (c) Kharasch, Read, and Mayo, *Chemistry and Industry*, **57**, 752 (1938); (d) Kharasch, May and Mayo, *J. Org. Chem.*, **3**, 175 (1938); (e) Kharasch, Jensen and Urry, *Science*, **102**, 128 (1945); Kharasch, Jensen and Urry, *THIS JOURNAL*, **68**, 154 (1946); Kharasch, Jensen and Urry, *ibid.*, **69**, 1100 (1947); Kharasch, Reinmuth and Urry, *ibid.*, **69**, 1105 (1947); (f) Kharasch, Urry and Jensen, *ibid.*, **67**, 1626 (1945); (g) Kharasch, Urry and Jensen, *ibid.*, **67**, 1864 (1945); (h) Sommer, Pietrusza and Whitmore, *ibid.*, **69**, 188 (1947); (k) Marvel, Dec and Corner, *ibid.*, **67**, 1355 (1945).

(2) (a) Kharasch and Gladstone, *ibid.*, **65**, 15 (1943); (b) Kharasch, McBey and Urry, unpublished work; (c) Kharasch, Smith and Urry, unpublished work.

Since an  $\alpha$ -bromine atom in an  $\alpha$ -bromo carboxylic ester is more susceptible to attack by a free methyl radical than is an  $\alpha$ -hydrogen atom of an ester<sup>3</sup> or any hydrogen atom in an aliphatic olefin, it should be possible, by using  $\alpha$ -bromo esters, to generate free ester radicals in olefinic solvents and to study their reactions with those solvents.

When a small amount of diacetyl peroxide (5-10 mole per cent.) is decomposed in a solution of octene-1 in ethyl bromoacetate a good yield of ethyl  $\gamma$ -bromocaproate and a small quantity of methyl bromide are obtained. The reaction presumably takes place according to the following scheme:



Step (1) is the initiating step. Steps (2) and (3) constitute a self-sustaining chain reaction; hence the number of condensations per free methyl radical is relatively large.

The requisites for such a self-sustaining chain reaction are as follows: (a) the free carboxylic ester radical and the olefin must be so constituted that they can condense rapidly (step 2); otherwise the concentration of the radical increases to the point where dimerization becomes a successfully competitive chain-breaker; (b) the nature of the bromo ester and the new radical produced by the addition of the free carboxylic ester radical to the olefin must be such as to permit the rapid transfer of a bromine atom from the former to the latter (step 3).

The type of condensation reaction described yields (as end-products) substituted  $\gamma$ -bromo esters. It has been successfully applied to bromo esters (both straight-chain and branched), and to  $\alpha$ -bromo dicarboxylic esters, but it fails with  $\beta$ -bromo esters. The reason for this failure is that the bromine atom in the  $\beta$ -position is but little affected by the carbalkoxy group; hence this atom is so strongly bound that condition (b) is not fulfilled.

Branching of the carbon skeleton of the ester in the neighborhood of the position  $\alpha$  to the carbalkoxy group shortens the chain length of the condensation reactions. Thus, under comparable conditions  $\alpha$ -bromoisobutyric and  $\alpha$ -bromoisobutyric

(3) It is noteworthy that in the  $\alpha$ -chlorinated acetic esters the chlorine atom is less active than the  $\alpha$ -hydrogen atoms.

valeric esters give poorer yields of condensation products than do the corresponding esters of the normal acids. If the amount of diacetyl peroxide is increased, the yield of the condensation product (formed from the bromo ester) increases. This fact indicates that some chain-breaking reaction operates with greater efficiency in the additions of branched free radicals to olefins than it does in the additions of the corresponding normal free radicals.

The question therefore arises whether this chain-breaking mechanism is a failure to meet condition (a) or a failure to meet condition (b). In order to obtain evidence on this point a number of experiments were carried out. It is to be borne in mind that octene-1 and the esters of  $\alpha$ -bromoacetic acid, when treated as described, give good yields of  $\gamma$ -bromo capric esters per unit of peroxide used; whereas octene-1 and the esters of bromoisobutyric acid give poor yields of  $\gamma$ -bromo- $\alpha$ , $\alpha$ -dimethylcapric esters. If diacetyl peroxide is decomposed in an octene-1 solution of a mixture of ethyl  $\alpha$ -bromoacetate and methyl  $\alpha$ -bromoisobutyrate, then the following results are to be anticipated. If the bromine atom in the bromoacetic ester is more easily attacked by the secondary alkyl free radical (step 3) than is the bromine atom in the bromoisobutyric ester then the chain should be carried mostly by the bromoacetate; here the predominant product should be ethyl  $\gamma$ -bromocaprate and this product should be obtained in good yield per unit of peroxide used. On the other hand, if the bromine atom in the isobutyric ester is more easily attacked, then the chain should be carried mostly by the bromoisobutyrate; here the predominant product should be methyl  $\gamma$ -bromo- $\alpha$ , $\alpha$ -dimethylcaprate and this product should be obtained in poor yield. Actually the reaction product, when converted to a lactone by distillation at 150° is principally a poor yield of  $\alpha$ , $\alpha$ -dimethyl- $\gamma$ -caprolactone. Even with an (undetected) impurity of 10% of  $\gamma$ -caprolactone in the reaction product, this result would still indicate that the bromine atom in the  $\alpha$ -bromoisobutyrate is at least eight times as easily attacked by secondary alkyl radicals (step 3) as is the bromine atom in the bromoacetate.

The experiment just described shows clearly that the  $\alpha$ -bromoisobutyric ester complies with condition (b) even better than does the bromoacetic ester. Hence the poor yields obtained from the  $\alpha$ -bromoisobutyrate must be due to inadequate compliance (on the part of this ester) with condition (a). Supporting this conclusion is the fact that when the  $\alpha$ -bromoisobutyric esters alone are added to olefins (under the condition stated) the reaction products always contain considerable quantities of tetramethylsuccinic esters. This result is exactly what would be predicted on the basis of the experiment cited. The free radical produced from  $\alpha$ -bromoisobutyric ester (step 1) adds so slowly to the olefin that it accumulates in

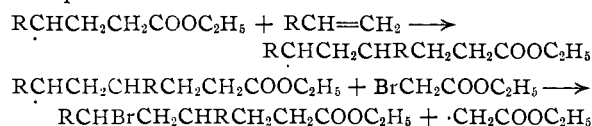
the solution to the point where dimerization effectively competes with the addition reaction.

Competition experiments similar to those already cited were carried out to determine the relative reactivities of the bromine atoms in ethyl bromoacetate and ethyl  $\alpha$ -bromo-*n*-butyrate. The condensation product was converted to the lactone, which proved to be a mixture of 45 mole per cent. of  $\gamma$ -caprolactone and 55 mole per cent. of  $\alpha$ -ethyl- $\gamma$ -caprolactone. This difference, (10%), is only slightly greater than the experimental error of the method. Hence, it may be concluded that, toward a secondary free alkyl radical, the bromine atom in ethyl  $\alpha$ -bromo-*n*-butyrate is only slightly more reactive than the bromine atom in ethyl bromoacetate. This result taken in conjunction with those already mentioned shows that, if only one hydrogen atom in bromoacetic ester is replaced by an alkyl radical, the reactivity of the bromine atom is but slightly increased. On the other hand, substitution of both hydrogen atoms by alkyl radicals greatly increases the reactivity of the bromine atom.

The nature of the alcoholic alkyl radical in the ester is not critical, so long as this radical contains no chain-breaking substituent. When tertiary butyl  $\alpha$ -bromopropionate is condensed with octene-1, the yield of condensation product is only slightly less than that obtained from the corresponding ethyl ester. In general, methyl esters appear to give slightly better yields than do ethyl esters; but, so far, there is no evidence to show whether the ethyl group exerts a chain-breaking effect by virtue of its active  $\alpha$ -hydrogen atom or whether it exerts a steric influence.

Varying the structure of the olefinic component has demonstrated that straight-chain aliphatic olefins with either terminal or non-terminal double bonds, participate successfully in the chain reaction. When styrene or ethyl acrylate are used under comparable conditions they yield products of moderate molecular weight rather than 1:1 condensation products. Judging from the ease with which these olefins undergo radical-induced polymerization, there can be little doubt that in the reactions tested condition (a) is fulfilled. Neither compound, however, fulfills condition (b) for the free radicals which they produce ( $C_6H_5CHCH_2$ - $CH_2COOC_2H_5$  and  $C_2H_5OCOCHCH_2CH_2COOC_2H_5$ , respectively) have so little ability to abstract a bromine atom from a molecule of  $\alpha$ -bromo ester that they cannot continue the reaction chain. On the other hand, these radicals can add to other molecules of styrene or ethyl acrylate and thus produce polymers. This latter type of reaction is of only slight importance when straight-chain aliphatic olefins are employed because (1) these olefins are not reactive enough to polymerize and (2) the radical produced from either of these (by addition of a free ester radical) is so reactive that it readily removes a bromine atom from the  $\alpha$ -bromo

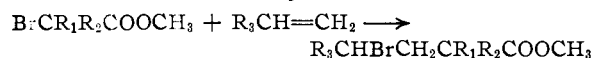
ester to continue the chain. But, even with these aliphatic olefins, there is always a small amount of residue left after removal of the 1:1 condensation product. This residue is probably a 2:1 condensation product formed as follows



The  $\gamma$ -bromo esters prepared in this study have been successfully converted to the corresponding  $\gamma$ -lactones both by alkaline hydrolysis followed by lactonization, and by direct thermal decomposition at 150–180°. This latter treatment results in the rapid formation of a  $\gamma$ -lactone and an alkyl bromide. Most of the  $\gamma$ -lactones hereafter described are new compounds; it was however possible to establish the identities of  $\gamma$ -valerolactone and  $\gamma$ -caprolactone by comparison with authentic samples of these compounds.

As a synthetic method, the free radical addition of an  $\alpha$ -bromo ester to an olefin is a simple one-step reaction which lengthens the carbon chain by two carbon atoms and simultaneously introduces a bromine atom in position gamma to the carboxyl group. The bromo compounds thus formed are not readily accessible by any other preparative method.

The over-all reaction where the double bond in the olefin is terminal may be formulated as



where the R's are either hydrogen atoms or alkyl groups.

### Experimental

The choice of the procedure to be used (as hereafter described) for the addition of bromo esters to olefins was governed by the physical properties of the olefin used. For gaseous olefins, a Pyrex pressure apparatus fitted with pressure stopcocks was employed; where the olefin was a liquid at the reaction temperature, no special equipment was needed.

It was found most convenient to add the diacetyl peroxide (dissolved in a small amount of bromo ester) in small portions (over a period of three to six hours) to a mixture of the olefin and the bromo ester contained in a flask held at a temperature of approximately 90°. When gaseous olefins were used, the bromo ester (held at 90°) was saturated with the olefin under a pressure of 40–55 pounds per square inch, absolute. The reactions were not markedly exothermic when the ratio of the reactants was as described. An inert atmosphere was maintained throughout all the reactions. Previous to the addition of the peroxide, air was always removed from the apparatus by flushing either with nitrogen or with the gaseous olefin.

Most of the addition products studied were stable when distilled *in vacuo* at pressures of 0.1–1.0 mm. However, in the cases of the  $\alpha$ -bromoisobutyrate,  $\alpha$ -bromoisovalerate, bromomalonnate, and bromosuccinate, some decomposition was noticed when the  $\gamma$ -bromo ester addition products were distilled in ordinary vacuum apparatus. The low values for the bromine content of some of the products (see Table I) are probably due to thermal decomposition of the  $\gamma$ -bromo esters to form the corresponding  $\gamma$ -lactones, by the elimination of ethyl or methyl bromide. In several of the experiments, molecular distillation

was used: here the bromine values and the saponification equivalents were satisfactory. To demonstrate the homogeneity of the condensation products the distillates were collected in many small fractions. The product was considered pure when both the boiling point and the index of refraction of successive fractions were constant. The following are typical procedures.

**Addition of Ethyl Bromoacetate to Octene-1.**—A solution of 27.4 g. (0.244 mole) of octene-1 in 160 g. (0.96 mole) of ethyl bromoacetate was treated with 3.1 g. (0.0254 mole) of diacetyl peroxide in 6.8 g. (0.041 mole) of ethyl bromoacetate. To isolate the addition product, the unreacted starting materials were removed by distillation at 20 mm. pressure. Distillation of the residue yielded 37 g. of ethyl  $\gamma$ -bromocaproate boiling at 93–94° (0.2 mm.),  $n_D^{20}$  1.4599. There was 1.6 g. of high-boiling residue.

**Addition of Ethyl Bromoacetate to Propylene.**—To 173 g. (1.03 mole) of ethyl bromoacetate which was kept saturated with propylene at 90° and 45 lb./sq. in. (absolute), was added (over a period of five hours) 1.8 g. (0.015 mole) of diacetyl peroxide dissolved in 8.0 g. (0.048 mole) of ethyl bromoacetate. The apparatus was vented three times during the addition of the peroxide to eliminate carbon dioxide. Distillation of the residue left after recovering unchanged ethyl bromoacetate yielded 22 g. of ethyl  $\gamma$ -bromo-*n*-valerate boiling at 103–104° (22 mm.),  $n_D^{20}$  1.4553. There was 1.5 g. of high-boiling residue.

**Formation of  $\gamma$ -Caprolactones from Ethyl  $\gamma$ -Bromocaproate. Proof of the Structure of Ethyl  $\gamma$ -Bromocaproate.**—Ethyl  $\gamma$ -bromocaproate (19.0 g., 0.0681 mole) was refluxed at 160–180° for two hours, during which time the external pressure was maintained at 55 mm. Volatile materials evolved during the pyrolysis were caught in a liquid nitrogen trap. Distillation of the residue gave 9.6 g. of  $\gamma$ -caprolactone (83% yield), b. p. 84° (0.2 mm.),  $n_D^{20}$  1.4489.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{18}\text{O}_2$ : saponification equivalent, 170. Found: sapon. equiv., 170.7; Br, 0.00.

This lactone was converted to the *p*-toluidide of  $\gamma$ -hydroxycaproic acid,<sup>4</sup> m. p. 133.4–134°. A sample of  $\gamma$ -caprolactone, made by the method of Fittig and Schneegans,<sup>5</sup> gave a *p*-toluidide, which melted at 133.5°. The mixture of the two toluidides melted at 133–134°. In the liquid nitrogen trap there was collected 6.1 g. of material which proved to be ethyl bromide, b. p. 38°, contaminated with hydrogen bromide. This ethyl bromide was further identified by conversion to ethyl mercuric bromide (m. p. 193°).<sup>6</sup>

In the distillation of the reaction mixture, 2.0 g. of a low-boiling fraction was collected. This material which gave a positive test for unsaturation when treated with a carbon tetrachloride solution of bromine, may possibly consist of unsaturated esters or acids formed by elimination of hydrogen bromide from the ethyl  $\gamma$ -bromocaproate during the heating period. The appearance of unsaturated material also accounts for the presence of hydrogen bromide in the cold trap.

In all cases the  $\gamma$ -bromo esters were converted to lactones by pyrolysis at 150–180°.

**Proof of the Structure of Ethyl  $\gamma$ -Bromo-*n*-valerate.**—The structure of the addition product, ethyl  $\gamma$ -bromo-*n*-valerate, obtained by the addition of ethyl bromoacetate to propylene, was proved in the following manner. A mixture of 10.6 g. of the addition product, 20 g. of sodium hydroxide and 30 cc. of water was heated under reflux for five hours. During this period the reaction mixture became homogenous. The solution was acidified with dilute hydrochloric acid, and then extracted with ether. The ether solution was washed with water and dried over anhydrous sodium sulfate. After the ether had been removed from the extract, a colorless liquid was obtained by distillation (4.0 g., b. p. 70° (6 mm.);  $n_D^{20}$  1.4328). This substance was identified as  $\gamma$ -valerolactone (80% yield)

(4) Koelsch and Tenenbaum, *THIS JOURNAL*, **55**, 3049 (1933).

(5) Fittig and Schneegans, *Ann.*, **227**, 79 (1885).

(6) Shriner and Fuson, "Identification of Organic Compounds," 2nd edition, p. 158.

TABLE I  
 EXPERIMENTAL DATA OF ADDITION REACTIONS<sup>c,d</sup>

Bromo ester, moles	Olefin, moles	Peroxide, moles	Addition product
Ethyl bromoacetate (1.00)	Octene-1 (0.244)	(0.025)	Ethyl $\gamma$ -bromocaprate
Ethyl $\alpha$ -bromopropionate (1.02)	Octene-1 (.265)	(.019)	Ethyl $\alpha$ -methyl- $\gamma$ -bromocaprate
<i>t</i> -Butyl $\alpha$ -bromopropionate (0.726)	Octene-1 (.196)	(.044)	<i>t</i> -Butyl $\alpha$ -methyl- $\gamma$ -bromocaprate
Ethyl $\alpha$ -bromo- <i>n</i> -butyrate (1.05)	Octene-1 (.25)	(.014)	Ethyl $\alpha$ -ethyl- $\gamma$ -bromocaprate
Ethyl $\alpha$ -bromoisobutyrate (0.838)	Octene-1 (.178)	(.022)	Ethyl $\alpha,\alpha$ -dimethyl- $\gamma$ -bromocaprate
Methyl $\alpha$ -bromoisobutyrate (0.739)	Octene-1 (.258)	(.027)	Methyl $\alpha,\alpha$ -dimethyl $\gamma$ -bromocaprate
Ethyl $\alpha$ -bromo-( <i>d</i> ) isovalerate (0.521)	Octene-1 (.132)	(.027)	Ethyl $\alpha$ -isopropyl- $\gamma$ -bromocaprate
Methyl $\alpha$ -bromoisovalerate (0.676)	Octene-1 (.206)	(.024)	Methyl $\alpha$ -isopropyl- $\gamma$ -bromocaprate
Dimethyl bromosuccinate (0.437)	Octene-1 (.089)	(.012)	Methyl $\alpha$ -carbomethoxy- $\gamma$ -bromocaprate
Diethyl bromomalonate (0.40)	Octene-1 (.44)	(.012)	Ethyl $\alpha$ -carbethoxy- $\gamma$ -bromocaprate
Ethyl bromoacetate (0.786)	Propylene 45 psia <sup>b</sup>	(.040)	Ethyl $\alpha$ -bromovalerate
Ethyl $\alpha$ -bromopropionate (0.602)	Propylene 45 psia <sup>b</sup>	(.025)	Ethyl $\alpha$ -methyl- $\gamma$ -bromovalerate
Ethyl $\alpha$ -bromoacetate (0.807)	Butene-2 45 psia <sup>b</sup>	(.029)	Ethyl $\beta$ -methyl- $\gamma$ -bromovalerate
Ethyl $\alpha$ -bromopropionate (0.656)	Isobutylene 45 psia <sup>b</sup>	(.015)	Ethyl $\alpha,\gamma$ -dimethyl- $\gamma$ -bromovalerate
Ethyl $\alpha$ -bromopropionate (0.944)	Styrene (.25)	(.023)	Styrene polymer
Ethyl $\alpha$ -bromopropionate (1.01)	Ethyl acrylate (.253)	(.019)	Acrylate polymer

by converting it to the amide of  $\gamma$ -hydroxy-*n*-valeric acid, m. p. 49–50°, according to the method of Boorman and Linstead.<sup>7</sup> The melting point of this derivative and the melting point of a mixture with the amide from an authentic sample of  $\gamma$ -valerolactone was 49–50°. For purposes of comparison,  $\gamma$ -valerolactone (b. p. 70–71° (6 mm.),  $n_D^{20}$  1.4328) was prepared by the reduction of levulinic acid according to the method of Schuette and Thomas.<sup>8</sup>

$\gamma$ -Valerolactone, 20.0 g., was converted into ethyl  $\gamma$ -bromo-*n*-valerate by dissolving it in 50 cc. of absolute ethanol and saturating the solution with hydrogen bromide at a temperature of 5°. The solution was allowed to stand for twenty-four hours at room temperature and was then resaturated with hydrogen bromide. After an additional twelve hours of standing at room temperature, an equal volume of water was added to the solution. The heavy organic layer which separated was extracted with ether, washed with dilute sodium bicarbonate solution, and dried over anhydrous sodium sulfate. Distillation of the residue through a 15-inch column packed with helices yielded pure ethyl  $\gamma$ -bromo-*n*-valerate, b. p. 78° (9 mm.)  $n_D^{20}$  1.4552, identical in all its properties with the ethyl bromoacetate-propylene addition product.

*Anal.* of the synthetic sample. Calcd. for C<sub>7</sub>H<sub>13</sub>O<sub>2</sub>Br: Br, 38.2. Found: Br, 38.3.

Boorman and Linstead<sup>9</sup> report for ethyl  $\gamma$ -bromo-*n*-valerate, b. p. 105–107° (20 mm.),  $n_D^{20}$  1.4533. This last figure is not in agreement with the observations here recorded. When the lactone was saturated with hydrogen bromide only once (instead of twice as above), the product was a mixture the constituents of which could not be separated by distillation through the packed column. This mixture had the following physical properties: b. p. 63–69° (6 mm.),  $n_D^{20}$  1.4460–1.4520.

**Tetramethylsuccinic Acid from the Reaction of Methyl  $\alpha$ -Bromoisobutyrate with Octene-1.**—By distillation of the product of the reaction between methyl  $\alpha$ -bromoisobutyrate and octene-1 (see Table I), a low-boiling fraction, 2.6 g., b. p. 40–95° (0.3 mm.) was separated. This fraction was saponified by refluxing it for one-half hour with an excess of alcoholic sodium hydroxide solution. All solvents were removed by distillation *in vacuo*. The residue was believed to be a mixture of the dry sodium salts of  $\gamma$ -hydroxyisobutyric acid,  $\gamma$ -hydroxy- $\alpha,\alpha$ -dimethylcapric acid and tetramethylsuccinic acid. The dry material was treated with 30 cc. of hot anhydrous ethyl alcohol in order to dissolve all the salts except the salt of the dicarboxylic

acid. The insoluble residue was collected on a filter, and added to 5 cc. of water, the solution was carefully acidified with sulfuric acid, and extracted with 15 cc. of ether. The ethereal solution was dried with anhydrous sodium sulfate, and the ether was then removed by evaporation. The white granular residue, 0.45 g., was washed well with ligroin and collected on a filter. The solid thus obtained melted at 190–192°; sublimation *in vacuo* did not raise its melting point. This melting point showed no depression when the material was mixed with an authentic sample of tetramethylsuccinic acid melting at 192°. The reported melting point of tetramethylsuccinic acid is 200°. However, it has been found that this melting point varies from 180 to 200°, depending upon the rate at which the sample is heated. This variation is due to the partial formation of the anhydride.

**Isolation and Identification of Methyl Bromide from the Reaction of  $\alpha$ -Bromo Esters with Octene-1.**—Methyl bromide was isolated and identified as a product in the condensations of octene-1 with dimethyl bromosuccinate, ethyl  $\alpha$ -bromopropionate, or ethyl  $\alpha$ -bromoisovalerate when these reactions were started by the decomposition of small amounts of diacetyl peroxide.

In the experiment with dimethyl bromosuccinate described in Table I, 0.012 mole of diacetyl peroxide was used for the initiation of the free radical chain. The methyl bromide was isolated by attaching a Dry Ice-ether trap to the reflux condenser of the reaction vessel. All volatile materials evolved during the addition of the peroxide solution were caught in this trap. At the conclusion of the reaction, the Dry Ice-ether was replaced by liquid nitrogen and the entire system was evacuated to 0.1 mm. The material collected in the trap was distilled into a vacuum line, weighed and identified by its molecular weight and vapor pressure. The molecular weight found was 92.4; that calculated for methyl bromide is 95. The vapor pressure at Dry Ice-ether temperature was 6.5 mm.; that reported<sup>11</sup> for methyl bromide is 5 mm. at –80.6°, and 10 mm. at –72.8°. The amount of methyl bromide isolated was 0.29 g. (0.0031 mole).

**Reaction of Ethyl  $\beta$ -Bromopropionate with Octene-1.**—Ethyl  $\beta$ -bromopropionate (188 g., 1.04 moles) was treated with 28 g. of octene-1 (0.25 mole) in the presence of 2.2 g. of diacetyl peroxide (0.019 mole). Removal of the unreacted starting materials left 4.0 g. of high-boiling residue. The compound formed under these conditions is diethyl  $\alpha$ -bromo- $\alpha'$ -methylsuccinate. This reaction will be discussed in a subsequent publication.

(7) Boorman and Linstead, *J. Chem. Soc.*, 578 (1933).

(8) Schuette and Thomas, *THIS JOURNAL*, 52, 3010 (1930).

(9) Boorman, Linstead and Rydon, *J. Chem. Soc.*, 575 (1933).

(10) Auwers and Meyer, *Ber.*, 23, 300 (1890).

(11) Stull, *Ind. Eng. Chem.*, 39, 517 (1947).

TABLE I (Continued)

°C.	B. p. Mm.	$n_D^{20}$	Addition product		Yield	°C.	B. p. Mm.	$n_D^{20}$	Lactone		Yield
			Found (calcd.)	Sapn. eq. Found (calcd.)					Found (calcd.)	Sapn. eq. Found (calcd.)	
93-94	0.2	1.4599	28.88 (28.67)	142.6 (139.5)	57.0%	84	0.2	1.4489	170.7 (180.0)	48%	
92	0.1	1.4570	26.92 (27.30)	148.2 (146.5)	77.0%	73-74	.02	1.4460	184.9 (184.0)	64%	
						73-74	.02	1.4460	185.0 (184.0)	49%	
108	0.6	1.4576	25.80 (26.05)	152.5 (153.5)	62.0%	114	.4	1.4480	193.7 (198.0)	47%	
"		1.4572	23.13 (26.05)	168.0 (153.5)	11.7 g.						
98-102	0.3	1.458	20.16 (27.30)		22.2 g.	83-84	.3	1.4436	198.2 (198.0)	24%	
"		1.4592	23.53 (24.92)	164.8 (160.5)	13.7 g.						
84-85	0.03	1.4608	25.83 (26.05)	154.1 (153.5)	46.0%	"		1.4508	210.0 (212.0)	41%	
"		1.4669	23.29 (23.73)	112.6 (112.3)	83.0%						
"		1.4572	21.82 (22.80)	119.8 (117.0)	74.0%	"		1.4504	121.2 (121.0)	58%	
82-83	8	1.4552	38.23 (38.2)	104.5 (104.5)	28.5 g.	70	6	1.4328		11 gr.	
82-84	9.5	1.4521	32.16 (35.80)	112.2 (111.5)	18.0 g.						
70-71	4	1.4588	35.27 (35.87)	12.2 (111.5)	19.2 g.	91-92	8	1.4346	114.2 (114.0)	10 gr.	
69-70	4	1.4520	33.84 (33.80)	124.4 (118.5)	103. g.						

<sup>a</sup> These products were molecularly distilled. <sup>b</sup> The amount of olefin added was not determined. <sup>c</sup> The over-all yield is based upon the amount of olefin used. <sup>d</sup> These reactions were heated between 70-80°.

**Competition Experiments. (A) Methyl  $\alpha$ -Bromoisobutyrate versus Ethyl Bromoacetate.**—A mixture of 49.2 g. of ethyl bromoacetate, 57.1 g. of methyl  $\alpha$ -bromoisobutyrate and 10.8 g. of octene-1 was heated for fourteen hours at 88°, in the presence of 1.1 g. of diacetyl peroxide. After distillation of the unreacted materials, the residue, upon distillation at reduced pressure, gave 6.5 g. of a material which contained 9.65% bromine. This material was heated at 150-180° for two hours to convert it to the lactone. Upon distillation at reduced pressure a material was collected which had an index of refraction of 1.4436 at 20°.

*Anal.* Calcd. for  $C_{10}H_{18}O_2$ : saponification equivalent, 170. Calcd. for  $C_{12}H_{22}O_2$ : saponification equivalent, 198. Found: sapn. equiv., 197, 202.

**(B) Ethyl  $\alpha$ -Bromo-*n*-butyrate versus Ethyl Bromoacetate.**—A mixture of 50.8 g. of ethyl bromoacetate (304 mmoles), 59.7 g. of ethyl  $\alpha$ -bromo-*n*-butyrate (306 mmoles), and 11.6 g. of octene-1 (104 mmoles) was heated for fourteen hours at 83° in the presence of 1.18 g. of diacetyl peroxide (10 mmoles). After distillation *in vacuo* of the unreacted materials, a residue (23.9 g.) was obtained. This residue was a mixture of the two possible  $\gamma$ -bromo esters. To convert these  $\gamma$ -bromo esters to the lactones, the material was heated at 150-180° for three hours, and then subjected to distillation at reduced pressure (b. p. 73-75° (0.02 mm.),  $n_D^{20}$  1.4488).

*Anal.* Calcd. for  $C_{10}H_{18}O_2$ : saponification equivalent, 170. Calcd. for  $C_{12}H_{22}O_2$ : saponification equivalent, 198. Found: saponification equivalent, 184.6, 186.3.

**Preparation of  $\alpha$ -Substituted  $\gamma$ -Caprolactones.**—These substances were prepared by the addition of the appropriate  $\alpha$ -bromo esters to octene-1; in each instance the reaction product was distilled *in vacuo* to obtain the  $\alpha$ -substituted  $\gamma$ -bromocaproate formed. When these  $\gamma$ -bromocaproates were refluxed for two hours at 160-180°, alkyl halides were evolved, and  $\alpha$ -substituted  $\gamma$ -caprolactones were formed. These lactones were then distilled at reduced pressures. By following this procedure

1.  $\alpha,\alpha$ -Dimethyl- $\gamma$ -caprolactone was obtained from methyl  $\alpha$ -bromoisobutyrate and octene-1.

*Anal.* Calcd. for  $C_{12}H_{22}O_2$ : C, 72.7; H, 11.1. Found: C, 72.3; H, 11.0.

2.  $\alpha$ -Carbomethoxy- $\gamma$ -caprolactone was obtained from diethyl  $\alpha$ -bromomalonate and octene-1.

*Anal.* Calcd. for  $C_{13}H_{22}O_4$ : C, 64.4; H, 9.12. Found: C, 63.8; H, 9.0.

3.  $\alpha$ -Isopropyl- $\gamma$ -caprolactone was obtained from methyl  $\alpha$ -bromoisovalerate and octene-1.

*Anal.* Calcd. for  $C_{13}H_{24}O_2$ : C, 73.5; H, 11.3. Found: C, 73.0; H, 11.4.

TABLE II  
PHYSICAL CONSTANTS OF BROMO ESTERS USED

Bromo ester	Boiling point		$n_D^{20}$
	°C.	Mm.	
Ethyl $\alpha$ -bromoacetate	58-59	15	1.4489
Ethyl $\alpha$ -bromopropionate	58	16	1.4461
Ethyl $\alpha$ -bromobutyrate	63	12	1.4479
<i>t</i> -Butyl $\alpha$ -bromopropionate	62.2	15	1.4392
Ethyl $\alpha$ -bromoisobutyrate	59.9	18	1.4438
Methyl $\alpha$ -bromoisobutyrate	52.2	21	1.4509
Methyl $\alpha$ -bromoisovalerate			1.4530
Ethyl $\alpha$ -bromoisovalerate	73-74	12	1.4496
Dimethyl bromosuccinate	61	3	1.4630
Diethyl bromomalonate	123	20	1.4521
Methyl $\alpha$ -bromoisovalerate	64-65	11	1.4530
Ethyl $\alpha$ -bromopropionate	69.7	15	1.4578

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### Summary

Good yields of  $\gamma$ -bromo esters are formed by free-radical chain reactions between aliphatic olefins and  $\alpha$ -bromo carboxylic esters. These reactions involve the addition of radicals of the  $\dot{C}-COOCH_3$  type to the double bond. The chain is initiated by the thermal decomposition of diacetyl peroxide. The mechanism and necessary requisites for the chain reaction are discussed.