

The Radical Bromination Reaction of Ethylenecarbonate

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Abstract □ The reaction of ethylenecarbonate (I) with bromine was carried out in the presence of benzoylperoxide as radical initiator. The following several different esters being ring opened were obtained; bromoacetyl-bromoformate, (1-hydroxy, 1,2-dibromo)-ethyl bromoformate, (1-hydroxy, 1,2,2'-tribromo)-diethylcarbonate, 2-bromoethyl-tribromoacetate, (1-acetoxy, 1'-bromomethyl)-bromomalonate, 2-bromoethyl-bromoacetoxy-tribromoacetate.

Keywords □ Radical bromination, Ethylenecarbonate, Radical initiator, Ring opened ester, Benzoylperoxide Fragment, Daughter ion.

Autocatalytic reactions of ethylenecarbonate with alcohols, thiols, carboxylic acids and aromatic amines have been shown to give the corresponding 2-hydroxyethyl derivatives¹⁾, and reactions of (I) with nucleophiles such as alkali metal halides in aqueous ethylene glycol to give 2-substituted ethanols²⁾. Otherwise, the radical chlorination of (I) have been reported to give mono and dichloroethylenecarbonates³⁾, but the radical bromination of title compound have not been yet done. In view of these facts, the present author attempted the reaction of (I) by bromine and radical initiator. The results thus obtained will be described in this paper.

RESULTS AND DISCUSSION

The radical bromination of (I) was carried out in the presence of benzoylperoxide and by

adding bromine slowly at 130°. From the reaction mixture 5 fractions were obtained by fractional distillation.

The carbonyl stretching frequencies of these all fractions occurred in the region between 1725 and 1740cm⁻¹. For comparison there were giving $\nu_{C=O}$ of F-3, (I) and monochloroethylenecarbonate in Fig. 2. Since these carbonyl absorptions were lower than cyclic carbonates in frequency (1800 and 1833cm⁻¹ respectively), all these fractions were assumed to be ring opened esters.

This result, however, let me to the assumption regarding the reaction that bromo-radical convert to bromide ion in the initial stage of

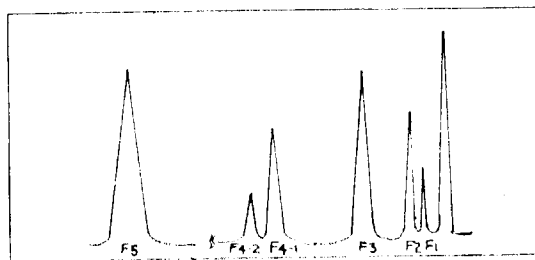


Fig. 1: The VPC pattern of the reaction mixture.

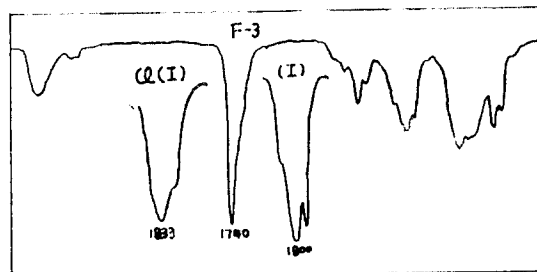
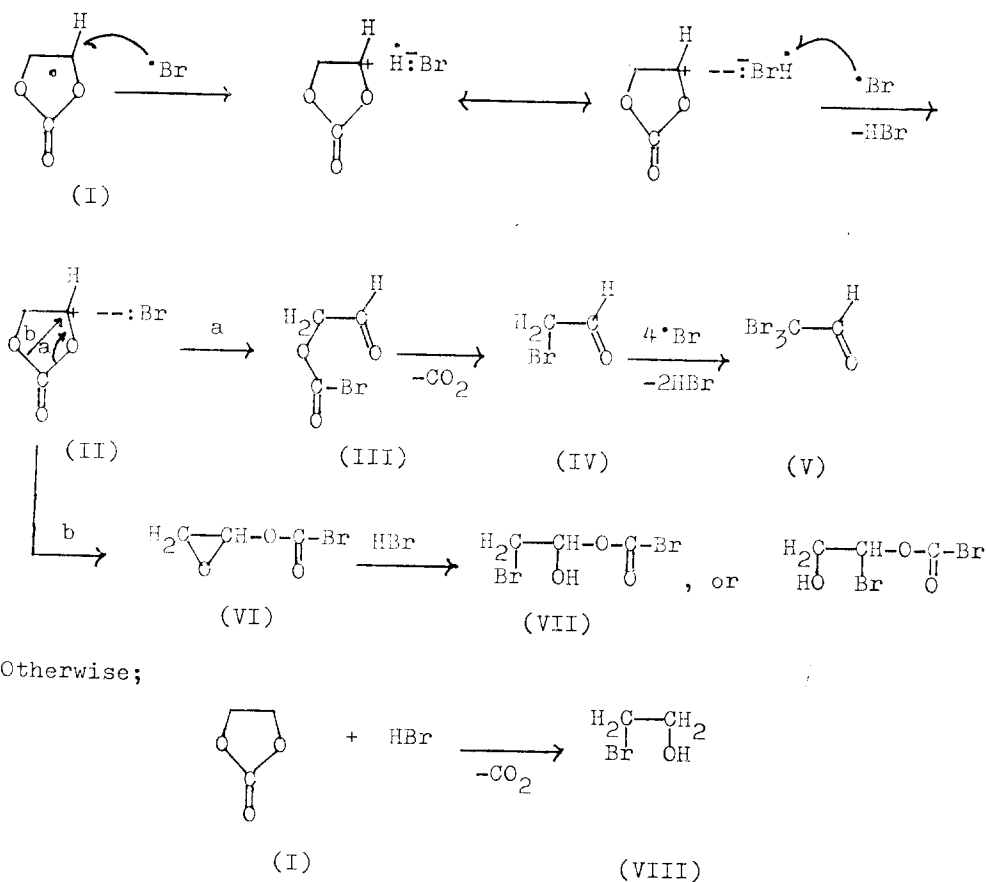


Fig. 2: The carbonyl frequencies of F-3 and cyclic carbonates.



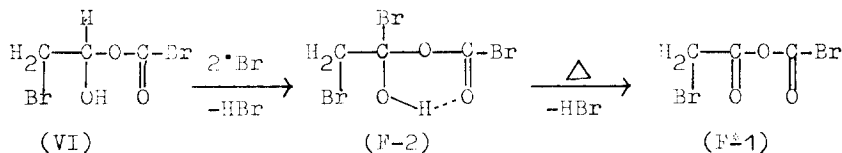
Scheme I: The paths of ring opening.

reaction, and then it react with (I) successively to afford the zwitter ion (II). It was based on the facts that in general, (I) was opened by ionic attacking species⁴⁾, and there was the difference in the reactivity arising from the nature of chloro and bromoradical⁵⁾. Accordingly, the following paths of ring opening would be expected.

The structural assignments of these fractions were accomplished on the basis of their NMR and GC-Mass spectral data, and simultaneously the purities of those were checked by VPC analysis.

Both F-1 and F-2 were contaminated with the others in small amounts, so the identification

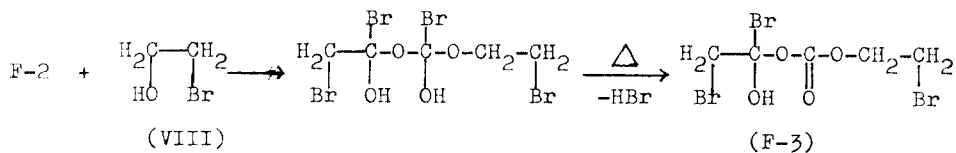
of each fraction has not been possible directly from the ratio of NMR signals. Fortunately, F-2 was separated into two layers during keeping it in a sealed tube, and by the checking of F-2 on VPC the lower was determined as F-1 and upper as F-2. A simple signal of F-1 was found at δ 3.82. And in Mass, mass number 216 ($M^+ - CO$), 108 ($^+OC - Br$), 94 ($^+CH_2 Br$) and 166 ($M^+ - \cdot Br$) were observed. Thus F-1 was identified as bromoacetyl-bromoformate. In F-2, the NMR signals at δ 2.25 (ratio: 2) and 9.77 (ratio: 3.8) and mass number of 309 ($M^+ - H_2O$), 108, 245 due to $BrCH - CBr - O - CO^+$ fragment and 173 ($CHBr_2$) were similarly



Scheme II

concluded to be (1-hydroxy,1,2-dibromo)-ethylbromoformate. In the NMR of F-2, the ratio 3.8 was likely responsible for a hydrogen bonding between F-3, HBr and H₂O. F-2 was considered to produce via an intermediate VI, by bromination of the tertiary hydrogen, and to be more or less stable through the hydrogen bonding as shown in scheme 2. But it was converted to F-1 accompanied the evolution of

hydrogen bromide gas by heat. According to VPC, it was proved to decompose into F-1 and seemingly HBr. F-3 was identified as (1-hydroxy,1,2,2'-tribromo)-diethylcarbonate by the following data: NMR; -CH₂Br at d 3.18, -CH₂CH₂Br at d 4.5 and 3.6, and -OH at 5.4., Mass; 309 (M⁺-ethyleneoxide), 108 (⁺CH₂-CH₂Br), 217 due to dibromoacetate ion, the daughters 173 and 94 (⁺CH₂Br).



Scheme III

F-3 was considered the product of the reaction of F-2 with ethylene bromohydrin, gave a hemiacetal and followed to dehydrogenbromide. As shown in Fig. 3, F-4 was contaminated with an 40%. From the absence of mass number 108 in F-4-2, it was guessed to include the ethylene moiety (at d 4.57 and 3.7) in the structure of F-4-1.

Looking into F-4-2, there were 209(M-CO), 122 due to monobromoacetyl ion, 59 due to acetate ion, 208(M⁺-CH₂Br), 149(O=C-C=O) and 68 daughter. In F-4-1, 324(M⁺-Br), 108, 280 due to tribromoacetyl ion and 252 daughter, 152(BrCH₂-CH₂-O-CO⁺) and 93(:CHBr).

Assuming from above data, F-4-1 was concluded to be 2-bromo-ethyl-tribromoacetate, and F-4-2 to be (1-acetoxy, 1'-bromomethyl)-bromo

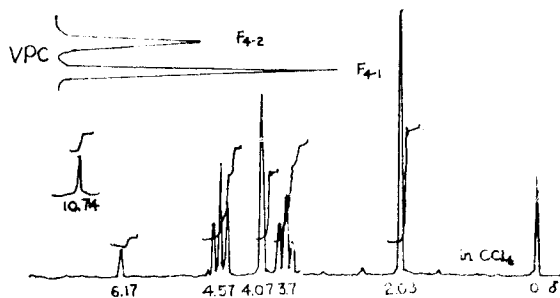


Fig. 3: The VPC and NMR patterns of F-4.

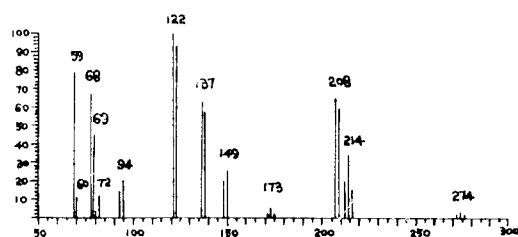
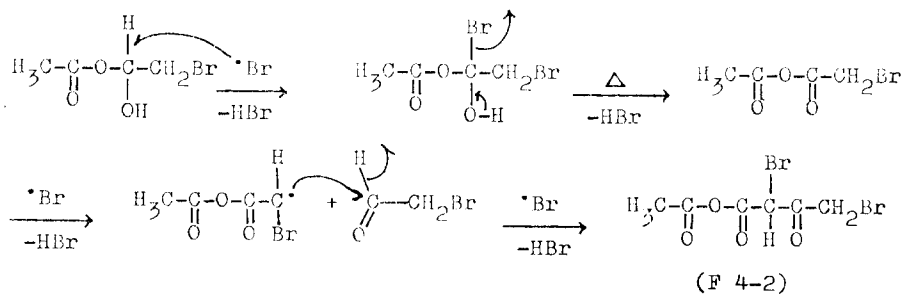
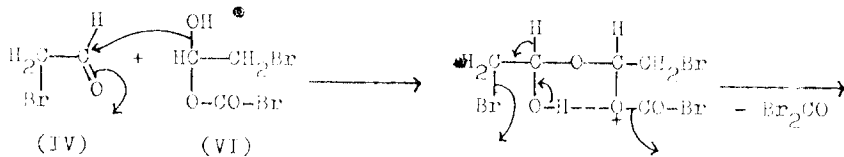
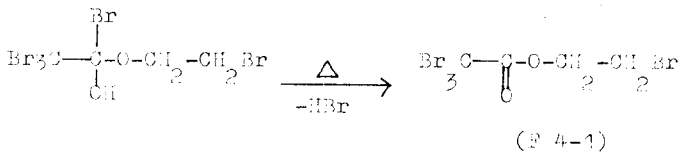
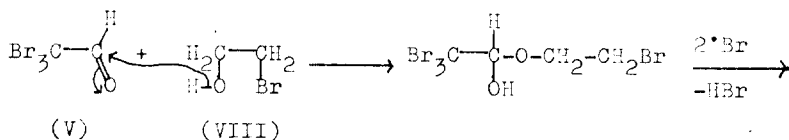
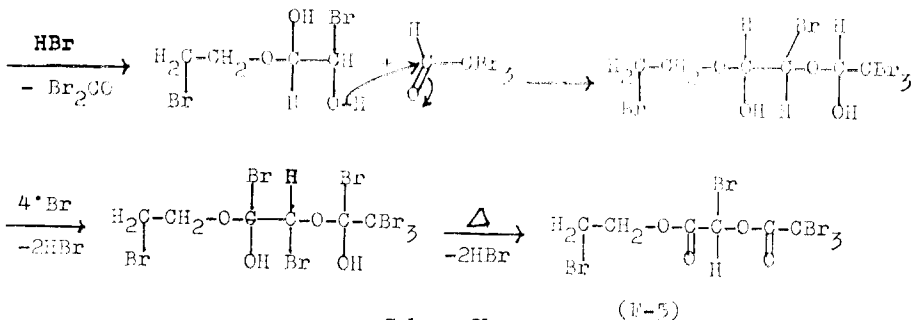
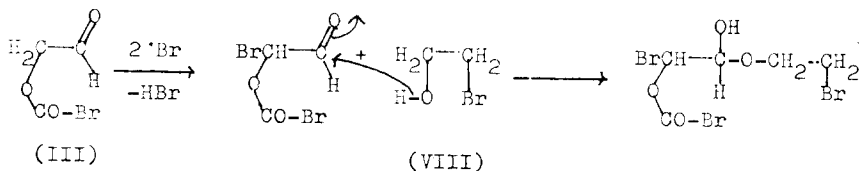


Fig. 4: The mass pattern of F-4-2.



Scheme IV



Scheme V

-malonate. The following plausible mechanisms for the formation of F 4-1 and F4-2 were suggested.

Finally, the NMR signals at 3.7 and 4.74 due to ethylene moiety and 6.1 (-O-CHBr-CO-), and mass numbers 384(M⁺-152), 152(BrCH₂-

$\text{CH}_2\text{-O-CO}^+$) and 108, 299 due to tribromoacetate ion and daughter ion 252, 167(cyclic ion of $\text{-CH}_2\text{-O-CO-CHBr-O-}$) and 94($^+\text{CH}_2\text{Br}$) were identified F-5 as 2-bromoethyl-tribromoacetate.

A hemiacetal produced from the reaction of brominated III with VIII may attack the carbonyl of another aldehyde to afford a other hemiacetal; subsequently the resultant hemiacetal may be brominated and followed by dehydrogenbromide to give F-5.

It was found that the carbonate ring had been retained in the radical chlorination without ring opening, but contrary to expectation, several different ring opened esters were formed in the bromination. It might be concluded that chlor-radical was unique active species in the chlorination, on the other hand, both bromo-radical and bromide ion played here on title compound to give several ring opened esters.

EXPERIMENTAL METHODS

All the boiling points were uncorrected. The VPC patterns were taken with Pye-unicam GC-240 (10% SE-30). The IR spectra were determined in neat liquid on a Beckmann AccuLab 4. The NMR spectral determinations were performed by using of a Varian EM 306, in carbontetrachloride as solvent. And determinations of spectra with Varian 3700 GC-MS instrument were performed by Mr. Jeen-Woo Park, Korea Ginseng and Tobacco Research Institute.

Ethylenecarbonate (I), bromine and benzoylperoxide were commercially purchased.

The Radical Bromination of (I)

In a 500 ml three-necked flask, provided with an efficient reflux condenser bearing an outlet tube connected to a gas absorption trap

and a dropping funnel, the stem of which extended to nearly the bottom of the flask, was placed 132g (1.5 moles) of (I).

Small amounts of phosphorous pentoxide was placed on the glass filter plate of the dropping funnel to dry the bromine. The flask was heated in an oil bath maintained at 125-135°. 6.4g of benzoylperoxide and 288g (98ml., 1.8 moles) were added in the following manner; A 0.4g portion of benzoylperoxide was added through the side neck to the stirred (I) per 30 minutes. From the dropping funnel the dried bromine was added dropwisely so that the bromine vapors did not transverse the condenser. The proceeding of reaction was checked by VPC per 2 hrs. After the bromine has been added (it required 8-9 hrs), nitrogen gas was passed into the reaction mixture in order to drive out the remaining hydrogen bromide. The resultant yellowish brown liquid was fractionated under reduced pressure, and 5 fractions were obtained.

Bromoacetyl-bromoformate (F-1)

Yield: 15g, BP: 105-106°/760 torr., IR: 1725 ($\nu_{\text{C=O}}$) and 585 cm^{-1} ($\nu_{\text{C-Br}}$), NMR: d 3.82(s, $\text{-CH}_2\text{Br}$), Mass: m/e 216($\text{M}^+\text{-CO}$), 108 (base, $^+\text{O}\equiv\text{C-Br}$), 166($\text{M}^+\text{-Br}$), 122(-CO_2) and 94(-CO),

(1-Hydroxy, 1,2-dibromo)-ethyl-bromoformate (F-2)

Yield: 20g, BP: 66-68°/70 torr., IR: 1725 ($\nu_{\text{C=O}}$) and 587 cm^{-1} ($\nu_{\text{C-Br}}$), NMR(in acetone- D_6): d 2.25(2H, s, $\text{-CH}_2\text{Br}$), 9.77(4H, s, due to hydrogen bonding, OH) and D_2O exchange(9.77 \rightarrow 7.17), Mass: m/e 309($\text{M}^+\text{-H}_2\text{O}$), 108(base, $^+\text{O}\equiv\text{C-Br}$), 121(BrCH=CO) and 93 (:CHBr), 245($\text{BrCH-CBr-O-C}\equiv\text{O}^+$), 201(-CO_2)

and 173($^+\text{CHBr}_2$),

(1-Hydroxy,1,2,2'-tribromo)-diethylcarbo-

nate (F-3)

Yield: 32g., BP: 81-84°/45 torr., IR: 1740 ($\nu_{C=O}$) and 550 cm^{-1} (ν_{C-Br}), NMR; δ 2.18 (2H, s, $-\text{CH}_2\text{Br}$), 3.6 (2H, t, J 6.0 Hz, CH_2Br of $-\text{CH}_2-\text{CH}_2\text{Br}$), 4.5 (2H, t, J 6.0 Hz, CH_2 of $-\text{CH}_2-\text{CH}_2\text{Br}$), 5.4 (1H, s, OH), Mass: m/e 309 (M-ethyleneoxide), 108 (base, $^1\text{CH}_2-\text{CH}_2\text{Br}$), 217 ($\text{Br}_2\text{CH}-\text{COO}^+$), 173 ($-\text{CO}_2$) and 137 ($-\text{Br}$), 168 ($\text{Br}-\text{CH}_2-\text{CH}_2-\text{O}-\text{COO}^+$), 94 ($^+\text{CH}_2\text{Br}$),

F-4. As described in results and discussion, it was a mixture of F 4-1 and F 4-2, so the NMR and Mass data of those were written under their titles separately.

Yield: 22.5g., BP: 118-122°/10 torr, IR: 1735 ($\nu_{C=O}$) and 560 cm^{-1} (ν_{C-Br}),

2-Bromoethyl-tribromoacetate (F 4-1)

NMR: δ 3.7 (2H, t, J 6.0 Hz, CH_2Br of $-\text{CH}_2-\text{CH}_2\text{Br}$), 4.57 (2H, t, J 6.0 Hz, CH_2 of $-\text{CH}_2-\text{CH}_2\text{Br}$), Mass: 324 ($\text{M}^+ - \text{Br}$), 108 (base, $^+\text{CH}_2-\text{CH}_2\text{Br}$), 280 ($^+\text{O}=\text{C}-\text{CBr}_3$) and 252 ($^+\text{CBr}_3$), 152 ($\text{BrCH}_2-\text{CH}_2-\text{O}-\text{C}\equiv\text{O}^+$) and 93 ($:\text{CHBr}$),

(1-Acetoxy, 1'-bromomethyl)-bromomalonate (F 4-2)

NMR: δ 2.03 (3H, s, $-\text{CO}-\text{CH}_3$), 4.07 (2H, s, $-\text{CO}-\text{CH}_2\text{Br}$), 6.17 and 10.74 (1H, each s, $-\text{CO}-\text{CHBr}-\text{CO}-$, due to keto-enol tautomer), Mass: m/e 274 ($\text{M}^+ - \text{CO}$), 122 (base, $\text{BrCH}_2-\text{C}^+=\text{O}^+$),

59 (CH_3-COO^+), 214 ($\text{BrCH}-\text{CHBr}$), 149 ($\text{OC}-\text{CO}$) and 68, 208 ($\text{M}^+ - \text{CH}_2\text{Br}$), 137 ($\text{BrCH}-\text{C}=\text{O}$),

2-Bromoethyl-bromoacetoxy-tribromoacetate (F-5)

Yield: 79g., BP: 130-134°/5 torr., IR: 1740 ($\nu_{C=O}$) and 570 cm^{-1} (ν_{C-Br}), NMR: δ 3.7 (2H, t, J 6.0 Hz, CH_2Br of $-\text{CH}_2-\text{CH}_2\text{Br}$), 4.7 (2H, t, J 6.0 Hz, CH_2 of $-\text{CH}_2-\text{CH}_2\text{Br}$), 6.1 (1H, s, $-\text{O}-\text{CHBr}-\text{CO}-$), Mass; m/e 389 ($\text{M}^+ - 152$), 152 ($\text{BrCH}_2-\text{CH}_2-\text{O}-\text{C}\equiv\text{O}^+$), 108 (base, $^+\text{CH}_2-\text{CH}_2-\text{Br}$), 299 ($\text{Br}_3\text{C}-\text{COO}^+$) and 252 ($^+\text{CBr}_3$), 167 (cyclic ion of $-\text{CH}_2-\text{O}-\text{CO}-\text{CHBr}-\text{O}-$),

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