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Synthesis of Ethylene Glycol Acetates Catalyzed by Potassium Iodide and Metal Acetate1)

Kazuo SHIMIZU* and Juichi IMAMURA
National Chemical Laboratory for Industry, Yatabe-machi, Tsukuba-gun, Ibaraki 305

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The catalytic activities of various kinds of binary systems consisting of KI and metal acetate were tested in liquid phase oxidation of ethylene in acetic acid at various pressures. KI–$Mn(OCOCH_3)_2$ was found to be the most reactive system and a new material, $CH_3COOCH_2CH_2OCOCH_2OCOCH_3$, was formed as a major by-product. It was also found that the main product at an early stage of the reaction was ethylene glycol monoacetate, from which other products were formed consecutively. It is considered that catalytic reaction does not proceed *via* ICH_2CH_2I, but *via* ICH_2CH_2OH which is formed by the oxidation of ethylene with HIO. On the basis of the rate equation and the results under various reaction conditions, a mechanism of the KI–$Mn(OCOCH_3)_2$-catalyzed reaction has been proposed.

At present, most of ethylene glycol is commercially manufactured by hydration of ethylene oxide. However, the total yield of ethylene glycol from ethylene is relatively low, because the selectivity of ethylene oxide production, in the vapor-phase oxidation of ethylene, is not so high.2) Therefore, other new methods of ethylene glycol synthesis, without ethylene oxide as an intermediate, have been proposed by several companies.2) Halcon International has developed a new process *via* ethylene glycol mono- and diacetates which are easily hydrolyzed to ethylene glycol and acetic acid.3) This process involved the acetoxylation of ethylene with KI-metal acetate catalyst. It recently attracted special interest because of the mild oxidizing conditions. Until now, however, the mechanism of this acetoxylation has not been published in detail. The authors have now studied the reaction mechanism and the results are published in this paper.

Experimental

Materials. The metal salts and acetic acid employed were all of a guaranteed grade and the ethylene and oxygen used were of a reagent grade; all were used without further purification.

Apparatus and Procedures. The reaction was performed in a closed system at higher pressure. A titanium-lined autoclave (300 ml) equipped with a magnetic stirrer and a thermocouple was used in conjunction with a pressure controller and a reservoir (469 ml) which was kept at 40 °C. The pressure inside the reservoir was measured by a strain gauge. The ethylene and oxygen gaseous mixture in a pressure ratio of 2 : 1 was preliminarily stored in this reservoir.

A mixture of the catalyst components and acetic acid was placed in the reaction vessel; the vapor phase was replaced with nitrogen, and the vessel was heated to the reaction temperature. At first, ethylene was introduced into the vessel until the desired pressure was obtained and then the mixture of ethylene and oxygen from the reservoir was introduced through the pressure controller until the pressure inside the vessel reached the reaction pressure. The gaseous mixture which decreased in pressure by dissolution and reaction was supplied continuously from the reservoir. Accordingly, the pressure inside the reaction vessel was held constant during the period of reaction.

The amount of mixed gas absorbed was measured by observing the pressure decrease inside the reservoir. The "reaction rate" means hereinafter the rate of pressure decrease during the initial stage of the reaction.

Identification and Analysis. Reaction products were identified by comparing their GC–MS(EI, CI) (JEOL, JMS-D300) and NMR (^1H, ^{13}C) (JEOL, JNM-FX100) spectra with those of authentic samples, and their amounts were determined by gas chromatography with a Shimadzu GC-4BT chromatograph (3m × 3 mm column packed with 20% Silicone DC-550 on Chromosorb WAW DMCS, from 60 to 170 °C, and 2 m × 3 mm column packed with Porapak Q, from 180 to 237 °C, He 40 ml/min). *o*-Dichlorobenzene was used as an internal standard.

Results and Discussion

Reaction Products. The major reaction products were ethylene glycol monoacetate (MA), ethylene glycol diacetate (DA), ethylene glycol (EG), $AcOCH_2CH_2OCOCH_2OH$ (**1**) (Ac means CH_3CO), $HOCH_2CH_2OCOCH_2OAc$ (**2**), $AcOCH_2CH_2OCOCH_2OAc$ (**3**), and $ICH_2CH_2OCOCH_2OAc$ (**4**)—the latter four will be designated the "higher boiling products." **3** was the new material with bp 219—220 °C; MS (70 eV), *m/e* (rel intensity), 174(13), 132(12), 131(12), 101(100), 87(18), and 73(16); MS (CI, NH_3) *m/e*=222, MS (CI,

Table 1. Product distibution for the oxidation of ethylene catalyzed by potassium iodide and different metal acetates

Catalyst Metal salts/mmol	Yield/g		
	DA	MA	EG
KI–$MnOA(c)_2\cdot 4H_2O$	1.38	0.60	0
–$Ce(OAc)_3\cdot H_2O$	1.26	0.65	0
–$Cr(OAc)_3\cdot H_2O$	0.70	0.29	≈0
–$Co(OAc)_2 4H_2O$	0.46	0.12	0
–$Cu(OAc)_2 H_2O$	0.69	0.22	0
–$Fe(OH)(OAc)_2$	0.48	0.17	0
–AgOAc	0.35	0.14	0
–$Ni(OAc)_2\cdot 4H_2O$	0.38	0.14	0
–$Zn(OAc)_2\cdot 2H_2O$	0.34	0.08	0

Reaction conditions; KI of 30 mmol, metal acetate of 5 mmol and acetic acid of 100 g (1.67 mol) were used, the ethylene pressure was 20 kg/cm^2, the oxygen pressure was 5 kg/cm^2, the reaction temperature was 140 °C and the reaction time was 60 min.

isobutane) $m/e=205$; $^{13}C-\{^1H\}$ NMR ($CDCl_3$) $\delta=171.2$, 170.0, 168.2(3CO), 63.5, 62.3, 61.1($3CH_2$) and 21.2, 20.8($2CH_3$).

Minor products were ICH_2CH_2OH, ICH_2CH_2OAc, CH_2I_2, $AcOCH_2CH_2OCH_2CH_2OAc$, $AcOCH_2CH_2OCH_2CH_2I$, and $ICH_2CH_2OCH_2CH_2OH$. The seven major products were taken into account; ordinarily the yields of the others could be ignored.

Selection of Catalysts. The oxidation of ethylene at an applied pressure was carried out with different catalyst systems. The reaction conditions and results are shown in Table 1. The products which are not listed in the table are omitted because of their negligible yields under these reaction conditions. As Table 1 shows, KI–$Mn(OAc)_2$ is the most active catalyst for the oxidation; accordingly, the reaction with KI–$Mn(OAc)_2$ catalyst system was investigated in detail.

Change of Product Yield with Reaction Time. The yields of the reaction products were determined at selected time intervals. As Fig. 1 shows, MA was the main reaction product at 15 min, the yields of MA, **2** and **4** were maximum at 60 min and those of DA, EG, **3** and **1** increased with reaction time.

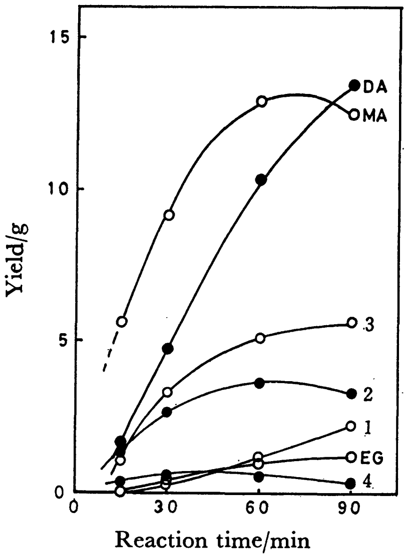


Fig. 1. Change of product yield with reaction time in the KI–$Mn(OAc)_2$-catalyzed reaction. Reaction conditions; KI$=$120 mmol, $Mn(OAc)_2\cdot 4H_2O=5$ mmol, AcOH$=$100 g, the pressures of ethylene and oxygen were 20 and 5 kg/cm^2, respectively, and the reaction temperature was 140 °C.

Effect of Oxygen Pressure. The reaction rate was of the first order in the oxygen pressure below 7.5 kg/cm and was independent of the pressure from 7.5 to 20 kg/cm^2 under the reaction conditions described in Fig. 2. The fact that the rate dependence on the oxygen pressure varied at 7.5 kg/cm^2 indicates that the reaction mechanism or the rate-determining step is different in the two regions. Figure 2 shows the effects of oxygen pressure on the product distributions after 90 min reaction. The yields of MA and **2** increased with an increase in the oxygen pressure, however, those of the other products were not affected greatly. The reaction was subsequently examined at an oxygen pressure of 7.5 kg/cm^2.

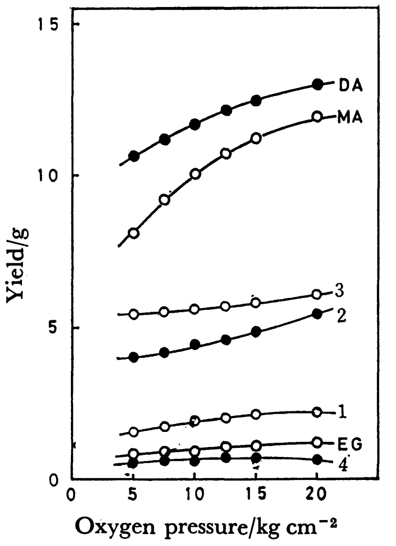


Fig. 2. Effect of the oxygen pressure on the product distributions. Reaction conditions; KI$=$120 mmol, $Mn(OAc)_2\cdot 4H_2O=1$ mmol, AcOH$=$100 g, the ethylene pressure was 20 kg/cm^2, the reaction temperature was 140 °C and the reaction time was 90 min.

Effect of Ethylene Pressure. The reaction rate was of the first order in the ethylene pressure below 25 kg/cm^2, and independent of the pressure from 25 to 30 kg/cm^2 under the reaction conditions; KI$=$100 mmol, $Mn(OAc)_2\cdot 4H_2O=5$ mmol, AcOH$=$100 g, the oxygen pressure of 7.5 kg/cm^2, the reaction temperature of 140 °C and the reaction time of 90 min. The reaction was subsequently investigated at an ethylene pressure of 20 kg/cm^2.

Effect of KI Concentration. The reaction rate was of the first order in the concentration of KI below 105 mmol/100 g AcOH under the reaction conditions destribed in Fig. 3; at concentrations above 120 mmol/100 g AcOH, a precipitate of KI was observed in the reaction mixture after the reaction. Figure 3 shows that the yields of DA and MA increased greatly with an increase in the KI concentration. On the basis of these results, the optimal concentration of KI for a fast reaction rate and selective formation of DA and MA is considered to be 120 mmol/100 g AcOH in the KI–$Mn(OAc)_2$-catalyzed reaction.

Effect of $Mn(OAc)_2$ Concentration. The reaction rate increased markedly with an increase in the $Mn(OAc)_2$ concentration between 0.1 and 1 mmol/100 g AcOH, and was independent of the concentration from 1 to 10 mmol/100 g AcOH under the conditions described in Fig. 4. Figure 4 shows that the $Mn(OAc)_2$ concentration hardly affected the product distributions. Therefore, the favorable region of concentration seems to be $1\leqq[Mn(OAc)_2]\leqq 10$ mmol/100 g AcOH.

Mechanism of the Reaction. Y. Ogata and K. Aoki have proposed a mechanism for the reaction of propylene with a mixture of iodine and peracetic acid.$^{5)}$ The mechanism of the KI–$Mn(OAc)_2$-catalyzed oxidation of ethylene is expressed as follows, by applying their mechanism to this reaction;

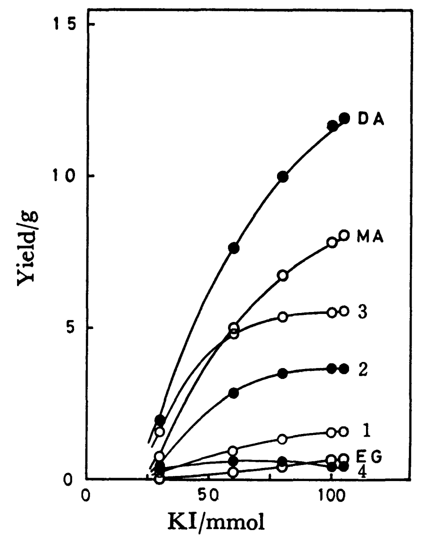


Fig. 3. Effect of the KI concentration on the product distributions. Reaction conditions; $Mn(OAc)_2\cdot4H_2O = 1$ mmol, AcOH = 100 g, the pressures of ethylene and oxygen were 20 and 7.5 kg/cm^2, respectively, the reaction temperature was 140 °C and the reaction time was 90 min.

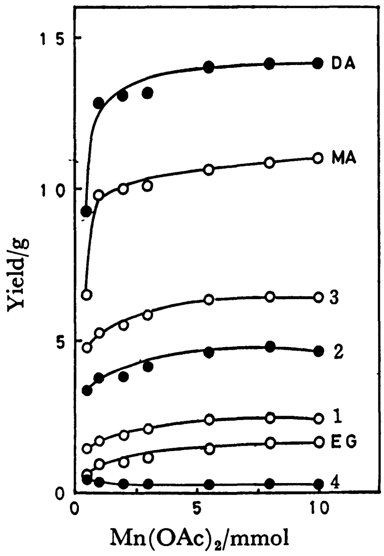
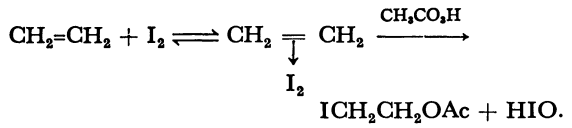


Fig. 4. Effect of the $Mn(OAc)_2$ concentration on the product distributions. Reaction conditions; KI = 120 mmol, AcOH = 100 g, the pressures of ethylene and oxygen were 20 and 7.5 kg/cm^2, respectively, the reaction temperature was 140 °C and the reaction time was 90 min.

Table 2. Reaction conditions and results

Run No.	Gas and pressure kg/cm^2	Catalyst/mmol and starting material/mmol[a]	Reaction time min	Yield/g DA	MA	EG	1	2	3	4	Other product
1	C_2H_4(20) O_2(7.5)	$Mn(OAc)_2\cdot4H_2O$(10)	90	≈0	≈0	≈0	0	0	0	0	
2	C_2H_4(20) O_2(7.5)	KI(120)	90	3.56	1.84	≈0	0.14	0.41	0.99	0.19	
3	C_2H_4(20)	I_2(60)[b]	90	0.43	0	0	0	0	0	0	ICH_2CH_2I(5.0) ICH_2CH_2OAc(1.86)
4	C_2H_4(20) O_2(7.5)	I_2(60)[b]	15	1.68	0.05	0	0	0	0	0	ICH_2CH_2I(3.2) ICH_2CH_2OAc(1.86)
5	C_2H_4(20) O_2(7.5)	I_2(60)[b]	90	5.26	0.59	0	0	0	0	0	
6	O_2(7.5)	ICH_2CH_2I(20),KOAc(120)[b] $Mn(OAc)_2\cdot4H_2O$(5)	15	0.37	0.07	0	0	0	0	0	
7	C_2H_4(20)	I_2(60),KOAc(120)[b] $Mn(OAc)_2\cdot4H_2O$(5)	90	1.09	0.15	0	0	0	0	0	
8	O_2(7.5)	ICH_2CH_2OH(60),KI(60)[b] KOAc(60),$Mn(OAc)\cdot{}_24H_2O$(5)	15	3.25	2.02	≈0	0	0	0	0	ICH_2CH_2OAc(0.75) $ICH_2CH_2OCH_2CH_2$-OH trace
9	C_2H_4(20)	KIO(11),[c]AcOH(60 g)[b]	15	0.19	0.29	0	0	0	0	0	
10	C_2H_4(20)	KIO_3(60)[b]	15	3.56	2.54	0	0	0	0	0	
11	O_2(7.5)	KI(120),$Mn(OAc)_2\cdot4H_2O$(5) DA(20 g), AcOH(80 g)	15	20	≈0	0	0	0	0	0	
12	O_2(7.5)	KI(120),$Mn(OAc)_2\cdot4H_2O$(5)	15	0	0	0	0	0	0	0	$AcOCH_2COOH$(0)
13	O_2(7.5)	KI(120),$Mn(OAc)_2\cdot4H_2O$(5) A mixture of EG acetates (30 g),[d] AcOH(70 g)	15	23.3	9.97	0.43	0.16	1.53	1.68	0.03	ICH_2CH_2OH trace ICH_2CH_2OAc trace
14	O_2(7.5)	KI(120),$Mn(OAc)_2\cdot4H_2O$(5) A mixture of EG acetates (30 g),[d] AcOH(70 g)	30	22.3	8.28	0.67	0.56	1.63	3.28	0.02	
15	C_2H_4(20) O_2(7.5)	KI(120),$Mn(OAc)_2\cdot4H_2O$(5) H_2O(10 g), AcOH(90 g)	15	1.50	5.20	0.03	0	0	0	0	ICH_2CH_2OAc(0.29) ICH_2CH_2OH trace

Acetic acid (100 g) was used unless the amount is specified. The reaction temperature was 140 °C. a) All except the amount expressed in gram. b) A Teflon-lined autoclave was used. c) 5% aq solution of KIO(40 g) was used. d) A mixture of DA(12.33 g), MA(10.46 g), EG(2.14 g), and acetic acid(5.07 g).



$$\mathrm{CH_2{=}CH_2 + I_2 \rightleftharpoons CH_2 \underset{\overset{\downarrow}{I_2}}{=} CH_2 \xrightarrow{CH_3CO_3H} ICH_2CH_2OAc + HIO.}$$

If the reaction proceeds by this mechanism, the main reaction product should be ICH_2CH_2OAc or DA which is formed from ICH_2CH_2OAc by the reaction with KOAc, because of the lack of water in the reaction mixture. However, Fig. 1 indicates that the initial reaction product is MA. Accordingly, this KI–Mn(OAc)$_2$-catalyzed reaction proceeds by a mechanism different from that proposed by them.

In order to study the mechanism of the KI–Mn(OAc)$_2$-catalyzed reaction, this reaction was investigated under various conditions. Table 2 shows the reaction conditions and the results obtained.

The catalytic reaction using Mn(OAc)$_2$ alone as a catalyst yielded practically no products (Run 1), however, the reaction using only KI yielded all of the products (Run 2). The reaction using I_2 alone in the absence of oxygen yielded ICH_2CH_2I and ICH_2CH_2OAc as the major products and DA as the minor one (Run 3). However, in the presence of oxygen the yields of the major two products decreased and those of DA and MA increased with reaction time (Runs 4, 5). The results of the I_2-catalyzed reactions indicate the following reaction pathway.

$$\mathrm{ICH_2CH_2I \longrightarrow ICH_2CH_2OAc \longrightarrow AcOCH_2CH_2OAc \longrightarrow AcOCH_2CH_2OH}$$

Indeed, ICH_2CH_2I yielded much more DA than MA (Run 6).

However, as Fig. 1 shows, MA was the main product in the beginning of the reaction and DA and EG yielded consecutively. These results imply that the catalytic reaction does not proceed *via* ICH_2CH_2I.[2] Indeed, ICH_2CH_2I, in spite of its stability under the reaction conditions (Runs 3, 4), was not detected by means of lpc in the reaction mixture.

The reaction in the absence of oxygen yielded very small amounts of products (Run 7). This result implies that oxygen does not reoxidize the reduced catalyst, but takes part in the main reaction. That is to say, oxygen and iodine (or iodine-containing compound) may form a compound (for instance, HIO) which gives a precursor of MA (Run 8), and that compound then reacts with ethylene to form ICH_2CH_2OH. The catalytic reaction seems to proceed as described above, actually, KIO and KIO_3 gave MA and DA in the reaction conditions (Runs 9, 10).

The assumption that the first reaction product is ICH_2CH_2OH is supported by the fact that a much greater amount of $BrCH_2CH_2OH$ is formed in the KBr–Mn(OAc)$_2$-catalyzed reaction than that of ICH_2CH_2OH in the KI–Mn(OAc)$_2$-catalyzed reaction. This could be explained in terms of the difference of the reactivities with KOAc between these two.

Formation-path of Higher Boiling Products. The reactions with and without Mn(OAc)$_2$ as a catalyst component showed the same product distributions (Fig. 4, Run 2). This result indicates that the Mn salt does not take part in the formation of the higher boiling products. Furthermore, neither the higher boiling products formed form DA (Run 11), nor acetoxyacetate yielded from acetic acid (Run 12).

However, the higher boiling products are formed in high yields from a mixture of ethylene glycol acetates (Runs 13, 14). In addition, as Fig. 1 shows, **2** is formed first among the higher boiling products with **3** secondly and **1** only later. These results suggest that the hydrogen of the acetoxyl groups of MA is at first substituted by iodine which is replaced by acetoxyl groups to form **2**; then **3** is formed by the acetoxylation of **2**, followed by the hydrolysis of **3** to form **1**.

On addition of water to the reaction mixture, it was found that the yields of the higher boiling products decrease markedly and that of MA increases (Run 15). These facts support the idea that iodine was converted to HIO according to the equilibrium ($I_2+H_2O=HIO+HI$) in the presence of water, and that HIO promoted the formation of MA.

The reaction rate may be expressed as follows under the following conditions; oxygen pressure above 7.5 kg/cm^2, ethylene pressure below 25 kg/cm^2, KI concentration between 30 and 105 mol/100 g AcOH, Mn(OAc)$_2$ concentration between 1 and 10 mmol/100 g AcOH.

$$V = -\mathrm{d}P/\mathrm{d}t = k[\mathrm{KI}][\mathrm{Mn(OAc)_2}]^{\circ}P_{\mathrm{C_2H_4}}P^{\circ}_{\mathrm{O_2}}.$$

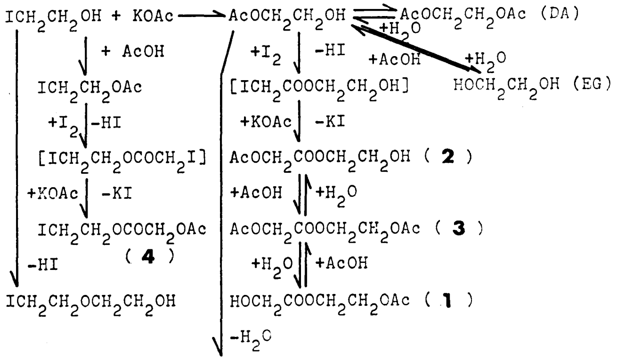
Furthermore, taking into account the above descriptions, the acidity of the reaction system and very little water in the reaction mixture in the beginning of the reaction, the catalytic reaction may be considered to proceed as follows;

$$\mathrm{KI + AcOH = HI + KOAc} \quad (1), \qquad \mathrm{4HI + O_2 = 2I_2 + 2H_2O} \quad (2)$$

$$\mathrm{2Mn(OAc)_2 + O_2 = (AcO)_2Mn{-}O{-}O{-}Mn(OAc)_2} \quad (3)$$

$$\mathrm{2HI + (AcO)_2Mn{-}O{-}O{-}Mn(OAc)_2 = 2HIO + 2Mn(OAc)_2} \quad (4)$$

$$\mathrm{CH_2{=}CH_2 + HIO \xrightarrow{slow} ICH_2CH_2OH} \quad (5)$$



The main reaction rate should be determined at the beginning of the reaction, because by-products are formed from the product of the main reaction. The above rate equation can be derived from this mechanism, by assuming that Eq. 5 is the rate-determing step, Eqs. 1, 3, and 4 are in equilibrium, P_{O_2} and [AcOH] disappear seemingly because of their sufficient amounts in the reaction mixture, and equilibrium 1 lies to the left because of the liberation of acidic HI in acetic acid.

Mn^{3+} and HIO seem to be the chemical species that are easy to form by oxidation from the viewpoint of redox potential, because the redox potentials of (HIO+

$H^+ + e = 1/2\ I_2 + H_2O$) and ($Mn^{3+} + e = Mn^{2+}$) in aqueous solution at 25 °C are 1.45 and 1.51 V, respectively,[6] and the values are not so high, although application of the values in aqueous solution to the reaction system under different conditions is questionable. Of course, the actual participating structures in the reaction system are uncertain. However, some speculation concerning a likely mechanism can be made on the basis of the known data. J. A. Elvidge and A. B. P. Lever first reported the Mn–O–O–Mn complex with Mn phthalocyanine in pyridine.[7] It is not unreasonable to consider chemical species such as $(AcO)_2Mn–O–O–Mn(OAc)_2$ and HIO even in acetic acid at higher temperature. The addition of HIO to olefines is well known to occur.[8]

Y. Ogata and K. Aoki might have observed the results of acetoxylation of the first reaction product, halohydrin, during their classical analytical operations. These required a much longer time than more rapid analytical methods such as gas chromatography.[5] Indeed, MA and ICH_2CH_2OH give corresponding acetates after a long time standing in acetic acid at room temperature.

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