TELOMERIZATION OF ETHYLENE WITH ESTERS OF DICHLOROACETIC AND TRICHLOROACETIC ACIDS

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UDC 542.952.6 + 547.313.2 + 547.464.2

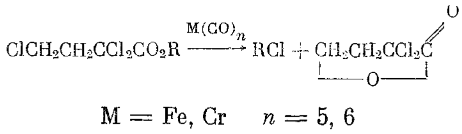
The telomerization of ethylene with esters of polyhaloacetic acids presents interest as a means of synthesizing higher dichloro- or trichlorocarboxylic acids of the even series. This reaction has not been studied for alkyl dichloroacetates. According to patent data [1], the reaction of dichloroacetic acid and ethylene under a pressure of about 1000 atm in the presence of benzoyl peroxide leads to the formation of a product whose average composition corresponds to a $C_2H_4:HCCl_2CO_2H$ ratio of 17.2 : 1. According to the data of Kharasch [2], the homolytic addition of ethyl dichloroacetate to 1-octene takes place via cleavage of a C—H bond in the alkyl group.

The telomerization of ethylene with esters of trichloroacetic acid under the influence of t-butyl peroxide has been described earlier in references [3-5]. Freidlina and Belyavskii [6] have briefly referred to the possibility of using iron pentacarbonyl to initiate such reactions. The reaction takes place according to scheme (1).

$$CCl_3CO_2R + nC_2H_4 \xrightarrow{\text{Initiator}} Cl(CH_2CH_2)_nCCl_2CO_2R \qquad (1)$$
$$n = 1, 2, 3 \quad R = CH_3, C_2H_5$$

In the present work we have studied reaction (1) initiated by iron pentacarbonyl or chromium hexacarbonyl in more detail, and have also effected the telomerization of ethylene with methyl dichloroacetate in the presence of t-butyl peroxide. The study of these reactions was carried out by gas chromatography, and new products were isolated and characterized.

We have established that chromium hexacarbonyl initiates the telomerization of ethylene with alkyl trichloroacetates similarly to iron pentacarbonyl. In both cases, lactones are also formed at a temperature of 140° and a pressure of 100-150 atm, together with esters of α,α,ω-trichlorocarboxylic acids. Thus, from the methyl and ethyl esters of trichloroacetic acid, along with products corresponding to scheme (1), there was obtained one and the same lactone, of composition $C_4H_4Cl_2O_2$, according to scheme (2).



$$ClCH_2CH_2CCl_2CO_2R \xrightarrow{M(CO)_n} RCl + \underbrace{CH_2CH_2CCl_2C(=O)}_{O} \qquad (2)$$
$$M = Fe, Cr \quad n = 5, 6$$

The lactone and the ester from which it is formed are not separated on chromatography on columns where silicone elastomer is used as liquid phase, but are easily separated when polyethylene glycol is used as the immobile phase. Besides the fact that one and the same product is formed under conditions where ethylene is telomerized with methyl or ethyl trichloroacetate, the structure of the lactone is confirmed also by its formation according to scheme (2) from known esters of α,α,ω-trichlorobutyric acid by heating the latter with iron pentacarbonyl at 140° for 4-5 h. According to the literature [7], esters of α,α-disubstituted ω-chlorovaleric acids easily form lactones on heating with iron salts.

Besides α,α-dichlorobutyrolactone, the formation of a second, higher-boiling lactone (L-2) took place in both cases, which corresponded in composition to a lactone from the ester of α,α,ω-trichlorocaproic acid (the telomer with n = 2). However, it appeared unlikely that an ester of trichlorocaproic acid would undergo cyclization according to a scheme analogous to (2) under the conditions of the experiment. Actually, a known sample of an α,α,ω-trichlorocaproic ester was not transformed into a lactone under the conditions for cyclization of α,α,ω-trichlorobutyric esters.

Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, No. 11, pp. 2474-2478, November, 1967. Original article submitted February 27, 1967.

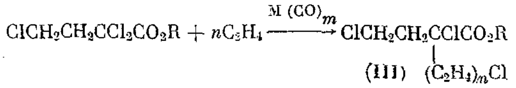
TABLE 1

$M(CO)_n$	Starting ester	Maximum pressure, atm.	Yield of reaction products, mole, %				Residue, wt. %
			$n = 1$	L-1	$n = 2$	L-2	
$Cr(CO)_6$	$CCl_3CO_2CH_3$	90	43.0	11.0	5.6	2	6.8
$Fe(CO)_5$	$CCl_3CO_2C_2H_5$	108	28.0	19.3	14.0	19.0	12.0
$Cr(CO)_6$	The same	146	25.6	30.6	7.6	22.6	13.7

TABLE 2

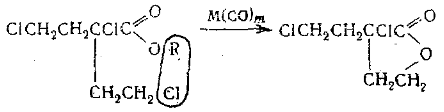
Compound	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR		Lit. ref.
				found	calculated	
$CCl_2CO_2CH_3$ C_2H_4Cl	85.5 (5)	1.4725	1.3905	41.54	41.42	—
$CCl_2CO_2C_2H_5$ C_2H_4Cl	98 (10)	1.4665	1.3256	45.90	46.16	[4.8]
$CCl_2CO_2CH_3$ $(C_2H_4)_2Cl$	86.5 (0,6)	1.4760	1.3100	50.28	50.77	—
$CCl_2CO_2C_2H_5$ $(C_2H_4)_2Cl$	113 (0.8)	1.4680	1.2413	55.45	55.39	[4.8]

In connection with this, we have proposed that in the presence of metal carbonyls one can effect a secondary telomerization of the ester of α,α,ω-trichlorobutyric acid (or its lactone), for example, according to scheme (3)



$$ClCH_2CH_2CCl_2CO_2R + nC_2H_4 \xrightarrow{M(CO)_m} \underset{(III)\ \ (C_2H_4)_nCl}{ClCH_2CH_2CClCO_2R} \qquad (3)$$

For compound (III) (n = 1), in the case of its closure to a lactone, the same five-membered ring is formed as in scheme (2).



(L-2).

A confirmation of the structure of lactone L-2 is the fact of formation of the very same product in telomerization of ethylene with the methyl or ethyl ester of trichloroacetic acid and the absence of ring closure of known esters of α,α,ω-trichlorocaproic acid when they are heated with carbonyls. Besides this, we have prepared the same lactone, L-2, by the reaction of methyl α,α,ω-trichlorobutyrate with ethylene in the presence of $Fe(CO)_5$.

It must be noted that the cyclization of α,α,ω-trichlorobutyric esters, and also their reaction with ethylene to form compounds containing a side chain (lactone L-2), are caused by the catalytic action of iron or chromium carbonyl and not by the temperature regime of the reaction. Thus, when reaction (1) is initiated by t-butyl peroxide at 140° (that is, at the same temperature as in the presence of the metal carbonyls), formation of lactones does not take place. Thus, the telomerization of esters of trichloroacetic acid initiated by metal carbonyls leads to a complex mixture of products, since, together with esters of α,α,ω-trichlorocarboxylic acids according to scheme (1), α,α-dichlorobutyrolactone and α-chloro-α-(β-chloroethyl)butyrolactone are formed.

The telomerization of ethylene with methyl dichloroacetate was carried out in the presence of t-butyl peroxide at 140° and 35 atm; here the formation of methyl esters of α,α-dichlorocarboxylic acids took place for the most part, and only traces α,ω-dichlorocarboxylic esters were formed. This shows that the reaction proceeds essentially with cleavage of a C—H bond in the acyl group; such a reaction course is probably connected with a larger stability of $\dot{C}Cl_2CO_2CH_3$ radicals compared with $H\dot{C}ClCO_2CH_3$ radicals.

TABLE 3

n	bp, °C (p, mm Hg)	Yield, % of total telomers	n_D^{20}	d_4^{20}	MR		Found, %		Calculated, %	
					found	calculated	C	H	C	H
1	93—94 (30)	25	1.4415	1.2447	36.32	36.58	35.20 35.34	4.59 4.65	35.10	4.68
2	92—94 (16)	40	1.4465	1.1648	45.61	45.82	42.03 42.04	6.07 6.13	42.20	6.03
3	110—113 (16)	10	1.4520	1.1122	55.06	55.06	47.76 47.66	6.89 6.96	47.50	7.05
$n>3$	120 (16)	20	—	—	—	—	—	—	—	—

The structure of the methyl esters of α,α-dichlorobutyric and α,α-dichlorocaproic acids was demonstrated by their hydrogenation [5] with hydrogen over Pd/$BaSO_4$ (5%) in the presence of the calculated amount of ammonia in methanol to the esters of butyric and caproic acid. The latter were shown to be identical with known samples by gas chromatography [5]. By special experiments it was shown that chlorine in the ω-position is not reduced under the conditions selected.

The presence of small amounts of methyl esters of α,ω-dichloro acids in the reaction mixture was demonstrated by gas chromatography by comparison with known samples, prepared by partial hydrogenation of methyl esters of α,α,ω-trichloro acids.

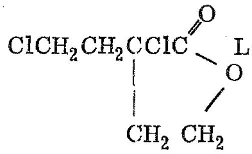
EXPERIMENTAL

Chromatography. For analysis of the reaction products obtained by telomerization of ethylene with esters of trichloroacetic acid we used a glass column 40 cm long, 3 mm in diameter, packed with Chromosorb W 0.15-0.2 mm in diameter; the immobile phase was 6% polyethylene glycol 15,000; temperature, 135°; carried gas, helium; detection was by thermal conductivity. By preliminary experiments it was shown that the esters of α,α,ω-trichloro acids and their lactones were separated under the selected chromatographic conditions. The composition of fractions obtained in experiments 1-3 (Table 1) was calculated approximately from the chromatograms. Then a known mixture of closely similar composition was prepared and the calibration coefficients obtained were used for exact calculation of the composition of the reaction mixture.

Analysis of the products of telomerization of ethylene with methyl dichloroacetate was carried out in a glass column 2 m long, of 4 mm diameter, with Chromosorb W of 0.25-0.5 mm diameter; immobile phase, 6% polyethylene glycol 4000; carrier gas, nitrogen; temperature, 100°; and with a flame ionization detector. As a second phase usable for identification of the compounds obtained, we used silicone elastomer.

Telomerization of Trichloroacetic Esters in the Presence of Metal Carbonyls. Experiments were carried out in a stainless steel rocking autoclave of 0.5 liter capacity. In the autoclave was placed 70 ml of the ester, and 0.2-0.4 g of iron or chromium carbonyl, and after displacement of the air with nitrogen, ethylene was introduced to a pressure of 65-70 atm. The autoclave was heated to 135-140° and kept at this temperature for 4 h. After the starting materials had been stripped, the reaction products were distilled in a column. Three fractions were isolated: I) bp 85-105° at 10 mm; II) bp 70-80° at 0.6 mm; III) bp 80-100° at 0.6 mm; and, finally, residue.

By gas chromatography it was established that fraction I was a mixture of $Cl(CH_2CH_2)_nCCl_2CO_2R$ (n = 1) and its lactone, L-1. Fraction III was a mixture of $Cl(CH_2CH_2)_nCCl_2CO_2R$ (n = 2) and the lactone



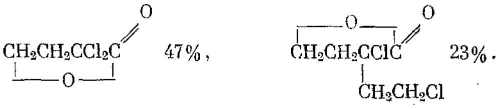
L-2; and intermediate fraction II contained all the compounds listed. The residue was not studied more closely.

In Table 1, we give the yields of products, calculated from the chromatograms obtained from fractions I-III.

By distillation in a column, from fraction I α,α-dichlorobutyrolactone, bp 80° at 1 mm, n_D^{20} 1.4790, d_4^{20} 1.4717, was isolated. Found %: C 30.97, 31.06; H 2.49, 2.49; Cl 44.94, 44.92; MR 29.71. $C_4H_4Cl_2O_2$. Calculated %: C 30.99; H 2.60; Cl 45.75; MR 29.29.

From fraction III by distillation in a column, α-chloro-α-(β-chloroethyl)bytyrolactone was isolated, bp 114° at 0.8 mm, n_D^{20} 1.4905, d_4^{20} 1.3625. Found %: C 39.33; H 4.45; Cl 38.92; MR 38.87. $C_6H_8Cl_2O_2$. Calculated %: C 39.37; H 4.40; Cl 38.74; MR 38.53.

Reaction of Methyl α,α,ω-Trichlorobutyrate with Ethylene. Into an autoclave of 10 ml capacity was placed 2 ml of $ClCH_2CH_2CCl_2CO_2CH_3$ plus 0.02 ml of $Fe(CO)_5$; and ethylene was introduced to a pressure of 55 atm; the mixture was heated at 135° for 5 h. The product was chromatographed and calculations were carried out as in the preceding experiment. According to the chromatographic data, the composition of the reaction mixture was: $CH_2Cl—CH_2CCl_2CO_2CH_3$, 30%;



Telomerization of Trichloroacetic Acid Esters with Ethylene in the Presence of t-Butyl Peroxide. Compounds of structure $Cl(C_2H_4)_nCCl_2CO_2R$ with n = 1 or 2 and R = CH_3 or C_2H_5 were prepared by the method of Rieche [4]. Constants of the substances obtained are given in Table 2. The analyses of all the enumerated compounds corresponded to the calculated values. The α,α,ω-trichlorocarboxylic esters prepared were used as standards for gas chromatography in setting up calibration mixtures. By gas chromatography it was established that α,α-dichlorobutyrolactone and α-chloro-α-(β-chloroethyl)butyrolactone were not among the reaction products.

Preparation of α,α-Dichlorobutyrolactone. In a flask provided with a reflux condenser, 2.5 g of methyl (or ethyl) α,α,ω-trichlorobutyrate and 0.02 ml of $Fe(CO)_5$ were heated to 140° for 4 h. The end of reaction was determined by the disappearance of the peak for the starting ester on chromatography under the conditions described above. The reaction product was distilled and was identified as α,α-dichlorobutyrolactone by gas chromatography.

Telomerization of Ethylene with Methyl Dichloroacetate. Into a steel rocking autoclave with an attachment for pumping in ethylene during the reaction process were charged 286 g of methyl dichloroacetate and 12 g of t-butyl peroxide. Air was displaced from the autoclave with ethylene and then ethylene was introduced to a pressure of 10 atm. The autoclave was heated at 140° for 4 h. The ethylene pressure was maintained at 25-35 atm. The starting ester was stripped off from the reaction mixture, and then a telomer fraction was isolated with a boiling range of 85° at 75 mm to 110° at 6 mm; wt. 56 g.

The conversion with respect to starting ester was 12-15%; similar fractions from four experiments were united and fractionated in a packed column (Table 3).

CONCLUSIONS

1. The telomerization of ethylene with methyl and ethyl trichloroacetates, catalyzed by iron pentacarbonyl, chromium hexacarbonyl,or t-butyl peroxide, has been studied.

2. Together with telomers of structure $Cl(CH_2CH_2)_nCCl_2CO_2R$, the formation of α,α-dichlorobutyrolactone and α-chloro-α-(β-chloroethyl)butyrolactone was observed; these result from catalytic cyclization under the influence of the metal carbonyls.

3. Esters of α,α,ω-trichlorobutyric acid react with ethylene under the influence of metal carbonyls to form α-chloro-α-(β-chloroethyl)butyrolactone.

4. Telomerization of ethylene with methyl dichloroacetate in the presence of t-butyl peroxide proceeds via cleavage of the acyl group C—H bond and leads to the formation of methyl esters of α,α-dichlorocarboxylic acids.

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