## REACTION OF $\alpha, \alpha, \omega$ -TRICHLORO- AND $\alpha, \alpha, \alpha, \omega$ -TETRACHLOROALKANES WITH ALKALI METAL ACYLATES IN APROTIC SOLVENTS

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Polychloroalkanes and -alkenes  $R(CH_2)_nCl$  (R =  $CHCl_2CH_2$ ,  $CCl_2$ =CH, n = 1, 3) in dipolar aprotic solvents - dimethylformamide (DMF), dimethylsulfoxide (DMSO), hexamethylphosphoramide (HMPA) - at 130-150°C react selectively at the  $CH_2Cl$ group with salts of carboxylic acids  $R'CO_2K(Na)$  to form dichloroesters  $R'CO_2$ .  $(CH_2)_nR$  (R =  $CHCl_2CH_2$ ,  $CCl_2$ =CH). In tetrachloroalkanes  $CCl_3CH_2(CH_2)_nCl$  (n = 1, 3, 5) under the same conditions the selectivity of the  $CCl_3$  and  $CH_2Cl$ groups relative to the nucleophile  $R'CO_2K(Na)$  is altered - unsaturated esters  $R'CO_2(CH_2)_nCH=CCl_2$  are formed in one stage with yields of 75-90%. Under the selected conditions, high conversion of polychloroalkanes to esters is attained 3 to 5 times more rapidly than in acid media. The structure of the ester obtained has been confirmed by their PMR spectra.

The nature of the solvent has a significant effect on the rate and even the direction of heterolytic reactions [1]. The preparation of esters from polychloroalkanes and -alkenes  $R(CH_2)_nC1$  (R = CHCl<sub>2</sub>CH<sub>2</sub>, CCl<sub>2</sub>=CH, CCl<sub>3</sub>CH<sub>2</sub>, n = 1, 3, 5) and salts of carboxylic acids R'CO<sub>2</sub>K(Na) is generally carried out in a medium of the corresponding acid with heating over a period of 12 to 50 h. Under these conditions, as also with liquid ammonia, alcoholates, and other nucleophilic reagents, the CCl<sub>3</sub> group does not react [2]. Esters  $R(CH_2)_nOC(O)R'$  are obtained in yields of 36-75% [2-4]. In the case of solid acids, a difficulty arises in the choice of solvent because in a reaction of RCl with the salts of one acid in a medium of another acid a mixture of esters of both acids is generally formed.

The reactions of acylates  $R'CO_2Na(K)$  with monochlorides RC1 (R = allyl,  $n-C_4H_9$ ,  $CH_2Si(OCH_3)_3$ ,  $CH_2CHCH_2O$  [5, 6],  $CH_2C_6H_5$  [5, 7]) and with dichlorides  $Cl(CH_2)_nC1$  (n = 2, 3) [6] have been studied in aprotic solvents (benzene, toluene, acetone, DMF, methyl ethyl ketone, etc.) and it has been shown that in DMF the reactions proceed at higher rates and with better yields of esters [5, 6, 8]. In the polychloropropanes  $CHCl_2CH_2CH_2Cl$  and  $CCl_3CH_2CH_2Cl$ , replacement of chlorine in the  $CH_2Cl$  group by iodine proceeds in a aprotic solvent (acetone) at a rate an order of magnitude higher than in alcohol [4].

The present work was concerned with the preparation of polychloroesters of carboxylic acids from polychloroalkanes and potassium (or sodium) acylates in aprotic solvents which permit an increase in the rate of the ester-forming reaction, and also with the clarification of the behavior of the polychlorinated groups  $CCl_3$ ,  $CHCl_2$ , and  $CCl_2=CH$  under the selected conditions.

We have studied the reaction of  $CHCl_2CH_2CH_2Cl$  (I),  $CCl_2=CH(CH_2)_3Cl$  (II),  $CCl_3(CH_2)_nCH_2Cl$  (IIIa-c) (n = 1, 3, 5), and  $CCl_3(CH_2)_4H$  (VI) with salts of acids  $R'CO_2K(Na)$  (R' =  $CH_3$ ,  $C_2H_5$ ,  $C_6H_5$ )\* in neutral and basic solvents (acetone, ethylacetate, dioxane, THF, DMF, DMSO, HMPA). For the example of the reaction of (I) with  $CH_3CO_2K$  it was found that the most promising solvents were DMF, DMSO, and HMPA. Under comparable conditions (120°C, 2 h) (I) reacted with  $CH_3CO_2K$  in DMF more rapidly (up to 98%) than in acetic acid (-10%) (Table 1, expts. 1, 2). Under preparative conditions, a 90% yield of 1,1-dichloro-3-acetoxypropane (V) was obtained from (I) and  $CH_3CO_2K$  in DMF (130-140°C, 5 h) (cp. [4]), and from 1,1,5-trichoropent-1-ene (II) a 75% yield of 1,1-dichloro-5-acetoxypent-1-ene (VI) (expts 3, 4)

 $K_{ioniz}$  for R'CO<sub>2</sub>H = (1.8, 1.3, 6.3)·10<sup>-5</sup> respectively.

A. N. Nesmeyanov Institute of Organometallic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2790-2793, December, 1990. Original article submitted September 1, 1989. TABLE 1. Conditions for the Reaction of  $R(CH_2)_nCl$  with Acylates  $R'CO_2K(Na) = CHCl_2CH_2$ , n = 1 (I),  $CCl_2=CH$ , n = 3 (II),  $CCl_3CH_2$ , n = 1 (IIIa), n = 3 (IIIb), n = 5 (IIIc), (130-150°C)

| Funt                | R(CH <sub>2</sub> ) <sub>n</sub> Cl |  | ]                      |                    |                  |                       |  |  |  |
|---------------------|-------------------------------------|--|------------------------|--------------------|------------------|-----------------------|--|--|--|
| No.                 | com-<br>pound                       | mmole  | R'CO₂K.<br>mmole       | DMF,<br>ml         | time,<br>h       | Conversion<br>RC1, %  | Yield of reaction<br>%   | 1 products,*                                   |  |
|                     |                                     |  |                        | Acylat             | e - P            | otassiu               | um acetate .   |  |  |
| 1<br>2 **<br>3<br>4 | (I)<br>(I)<br>(I)<br>(II)           | $ \begin{array}{c c} 0,7 \\ 0,7 \\ 10 \\ 25 \\ \end{array} $ | 0,8<br>0,8<br>11<br>30 | 1<br>1<br>15<br>60 | 2<br>2<br>5<br>6 | 98<br>10<br>100<br>90 | $CHCl_{2}CH_{2}CH_{2}OC(O)CH_{3}$ $CCl_{2}=CH(CH_{2})_{3}OC(O)CH_{3}$  | (V),90<br>(V),7<br>(V),92<br>(VIb),72          |  |
|                     |                                     |  | -                      | Pe                 | otassi           | um benz               | zoate  |  |  |
| 5                   | (I)                                 | 37   | 40                     | 20                 | 7                | 100                   | $CHCl_2CH_2CH_2OC(0)C_{u}H_5$  | (VII), 68                                      |  |
|                     |                                     |  |                        | Se                 | odium            | acetate               | <b>9</b> · ·   |  |  |
| 6                   | (IIIa)                              | 20   | 40                     | 16                 | 6                | 100                   | $CCl_2 = CHCH_2OC(0)CH_3$  | (VIa), 95                                      |  |
|                     |                                     |  |                        | Pot                | tassiu           | m propi               | ionate   |  |  |
| 7                   | (IIIa)                              | 18   | 32                     | 60                 | 6                | 100                   | $CCl_2 = CHCH_2OC(0)C_2H_5$  | (VIII), 85                                     |  |
|                     |                                     |  |                        | Po                 | otassi           | um acet               | ate  |  |  |
| <b>8 **</b><br>9    | (IIIa)<br>(IIIb)                    | 20<br>150  | 40<br>300              | 20<br>60           | 5<br>5           | 100<br>100            | $CCl_2 = CH(CH_2)_3OC(0)CH_3$  | (VIa), 90<br>(VIb), 75<br>(IXb), 20            |  |
| 10<br>11            | (IID)<br>(IIIS)                     | 30<br>100  | Ni1<br>200             | 20<br>60           | 5<br>5           | 10<br>100             | $\begin{array}{c} \text{CCl}_{2} = \text{CH}(\text{CH}_{2}) _{3}\text{CC}(0) _{1}\text{CH}_{3}\\ \text{CCl}_{2} = \text{CH}(\text{CH}_{2}) _{3}\text{Cl}\\ \text{CCl}_{2} = \text{CH}(\text{CH}_{2}) _{3}\text{OC}(0) _{1}\text{CI}_{3}\\ \text{COL}_{2} = \text{CH}(\text{CH}_{2}) _{3}\text{OC}(0) _{2}\text{CI}_{3}\\ \text{COL}_{2} = \text{CH}(\text{CH}_{2}) _{3}\text{OC}(0) _{3}\text{CI}_{3}\\ \text{COL}_{3} = \text{CH}(\text{CH}_{2}) _{3}\text{OC}(0) _{3}\text{CI}_{3}\\ \text{COL}_{3} = \text{CH}(\text{CH}_{2}) _{3}\text{OC}(0) _{3}\text{CI}_{3}\\ _{3}\text{CI}_{3} = \text{CH}(\text{CH}_{2}) _{3}\text{CI}_{3} = \text{CH}(\text{CH}_{2}) _{3}\text{CI}_{3} = \text{CH}(\text{CH}_{2}) _{3}\text{CI}_{3} = \text{CH}(\text{CH}_{2}) $ | (IAD), 20<br>(II), 7<br>(VIC), 72<br>(IXC), 47 |  |
| 12 ***<br>13        | (IV)<br>(IIIa)                      | 40<br>25   | 40<br>50               | 20<br>25           | 3<br>4           | 69<br>100             | $CCl_{2}=CH(CH_{2})_{3}H$  | (1XC), 17<br>(X), 60<br>(VIa), 48              |  |

\*Yields expressed based on GLC results of distilled products, in expts. 1, 2, and 8, on GLC results.

\*\*In expt. 2, solvent =  $CH_3COOH$ , in expt. 8, DMSO, in expt. 13, HMPA; in expts. 4 and 8 the acylate was sodium acetate.

\*\*\*In expt. 12, the initial alkane was  $CCl_3(CH_2)_4H$  (IV).

## $$\begin{split} \mathrm{CHCl_2CH_2CH_2CI} & \mathrm{(I)} + \mathrm{R'CO_2K} \rightarrow \mathrm{CHCl_2CH_2CH_2OC(O)R'} \\ \mathrm{R'} &= \mathrm{CH_3} & \mathrm{(V)}, \ \mathrm{C_6H_5} & \mathrm{(VII)} \end{split}$$

Potassium benzoate reacts with (I) in DMF in a similar manner. The ester  $CHCl_2CH_2CH_2OC(0)$ .  $C_6H_5$  (VII) is formed ~5 times more rapidly than in cyclohexanol [4] (expt. 5). Under the conditions of the reaction the  $CHCl_2$  and  $CCl_2=CH$  groups remain inert.

The tetrachloroalkanes  $CCl_3(CH_2)_nCH_2Cl$  (IIIa-c) react with potassium (sodium) acetate in DMF, DMSO and HMPA nonselectively - both chlorinated groups react, in contrast to the reaction taking place in acetic acid [2]. In this case the chlorine on the  $CH_2Cl$  group is replaced and dehydrochlorination of the  $CCl_3CH_2$  group occurs. As a result, at 100% conversion of chloroalkanes (IIIa-c), the unsaturated esters  $CCl_2=CH(CH_2)_nOC(0)CH_3$  (VIa-c), n = 1, 3, 5, are formed in one stage with yields of 75-90% (expts. 6, 8, 9, 11).



Tetrachloropropane (IIIa) in reaction with sodium acetate in DMF is almost completely dehydrochlorinated and converted into the ester  $CCl_2=CHCH_2OC(0)CH_3$  (VIa) (expts. 6, 8), and it reacts somewhat less actively with potassium propionate (expt. 7). The chloroalkanes (IIIb, c) also form 20-17%  $CCl_3CH_2(CH_2)_nOC(0)CH_3$  (IXb, c, n = 3, 5 respectively) (expts. 9, 11). The tetrachloroalkanes are not significantly dehydrochlorinated by dimethylformamide

| Com-                  | δ. (ppm /J <sub>C-H</sub> , Hz |                       |                           |              |                      |  |  |  |  |  |
|-----------------------|--------------------------------|-----------------------|---------------------------|--------------|----------------------|--|--|--|--|--|
| pound                 | C'                             | C <sup>2</sup>        | CH2O                      | со           | CH3C                 | (CH <sub>2</sub> ) <sub>n</sub>                |  |  |  |  |
| (V) *                 | 70,3                           | 42,2                  | 60,1                      | 169          | 20,4                 |  |  |  |  |  |
| (VIa)                 | 124,9                          | $\frac{130}{131}$     | <u>60,4</u><br><u>150</u> | 169          | $\frac{20}{129}$     |  |  |  |  |  |
| (VIb)                 | 120                            | $\frac{128}{160.5}$   | $\frac{63,2}{146,9}$      | 170,7        | $\frac{20,6}{130}$   | $\frac{26,6}{131}$ , $\frac{26,0}{129}$        |  |  |  |  |
| (VIc)                 | 119,7                          | <u>129,3</u><br>160   | <u>63,9</u><br>146,4      | 170,6        | $\frac{20,6}{129,3}$ | 29; 25; 28; 27,4                               |  |  |  |  |
| <b>VII)</b> *         | $\frac{70,0}{178,6}$           | 42,2                  | <u>60,7</u><br>149,9      | 165,7        | -                    | C <sub>6</sub> H <sub>5</sub> 132,9-128        |  |  |  |  |
| (VIII)                | 129,4                          | $\frac{126,4}{166,5}$ | $\frac{61,4}{149,9}$      | 173,6        | <u>9,9</u><br>128    | CH <sub>2</sub> C=0, $\frac{28,0}{128}$        |  |  |  |  |
| (IXb)<br>(IXc)<br>(X) | 99,5<br>99,9<br>119,7          | 54,5<br>54,4<br>129,7 | 63,6<br>64,1<br>-         | 170<br>170,9 | 20,8<br>20,0<br>13,4 | 27; 23<br>27,7; 25,4; 28,7; 26,0<br>21,3; 31,2 |  |  |  |  |

TABLE 2. <sup>13</sup>C NMR Spectra of Polychloroesters  $R(CH_2)_n OCOR'$  (V)-(IX) and Dichloroalkane (X)

\*cf. [4].

(expt. 10). The dehydrochlorinating reagent appears to be potassium acetate in DMF - from  $CCl_3(CH_2)_4H$  (IV), 60%  $CCl_2=CH(CH_2)_3H$  is formed after 3 h (expt. 12).

In HMPA, unsaturated esters are formed from tetrachloroalkanes and  $R'CO_2K$  in lower yield than in DMF. Some reaction of the HMPA with the reagents was noted. For example, in the reaction of (IIIa) with potassium acetate N,N-dimethylacetamide was formed in addition to the ester (VIa) (expt. 13).

Thus, potassium (sodium) acylates in dipolar aprotic solvents – DMF, DMSO, HMPA – as a result of the solvating effect of the solvent [1] apparently behave as strong bases relative to  $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes and are active esterification and dehydrochlorination reagents. One can obtain unsaturated esters  $CCl_2=CH(CH_2)_nOC(O)R'$  from  $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes in one step in high yields. Under the conditions selected, reactions of polychloroalkanes (alkenes) with salts of carboxylic acids take place more rapidly (by ~3-5 times) than in an acid medium and the desired esters are formed in yields of 60-90% at high conversions of the initial RC1. In these solvents it is possible to prepare esters directly from polychloroalkanes and salts of solid acids.

All the reaction products (V)-(X) were isolated in pure form and identified by GLC. The presence of  $CHCl_2$ ,  $CCl_3$ ,  $CH_3COO$ ,  $CH_3CH_2COO$ , and  $C_6H_5COO$  groups, and the  $CCl_2=CH$  group which was formed, was confirmed from the <sup>13</sup>C NMR spectra (Table 2), the <sup>13</sup>C chemical shifts and  $J_{C-H}$  of which were in agreement with known values (cf. [9, 10]).

## EXPERIMENTAL

GLC analyses were carried out on a LKhM-8MD chromatograph with a katharometer detector in a current of helium at 70-150°C on steel columns: 1) 1000  $\times$  3 mm with 5% SE-30, 2) 1000  $\times$  3 mm with 15% carbowax 20 M, 3) 2000  $\times$  9 mm with 15% silicone E-301 (for preparative purification of the products). The solid carrier was Chromaton N-AW, 0.16-0.20 and 0.20-0.25 mm.

<sup>13</sup>C NMR spectra were runt using 20-50% solutions of the individual compounds in CHCl<sub>3</sub> or CCl<sub>4</sub> relative to TMS ( $\delta$  scale) using the "J modecho" technique on a Bruker WP-200 SY instrument (50.31 MHz) with and without supression of C-H interaction (Table 2).

<u>Polychloroalkyl (or alkenyl) Esters of Carboxylic Acids</u>. The reactions were carried out in a stirred flask for 5-7 h at 130-150°C in the reaction suspension. The cooled mixture was diluted with water, or the liquid decanted from the precipitate, and the precipitate washed with chloroform. The organic portion was washed with water and the water extract with chloroform. The reaction products were separated by distallation in vacuum and purified by distillation in columns of 3-8 theoretical plates or by preparative GLC on column

+The authors wish to thank V. I. Dostovalov for running the NMR spectra.

(3). The difficulty in separating the reaction product from the solvent can be reduced if the reaction is carried out in a solvent whose boiling point is as different as possible from that of the product. The physical constants of the esters prepared correspond to known values [2-4]. Thus  $n_D^{20}$  (V) 1.4470, (VIb) 1.4700, (VIa), 1.4680, (VIc) 1.4700, (IXb) 1.4690, (IXc) 1.4675, (VII) 1.5300.

 $\frac{3,3-\text{Dichloroallylpropionate (VIII)}}{1.4600, \, d_4^{\,2\,0}} (200, \, d_4^{\,2\,0}) ($ 

For  $CCl_2$ =CHCH<sub>2</sub>OCOCH<sub>3</sub> (VIa) prepared from (IIIa): a) in DMSO (expt. 8). <sup>13</sup>C NMR spectrum ( $\delta$ , ppm, J<sub>C-H</sub>, Hz): 125.0(CCl<sub>2</sub>=), 123.9 (CH=, J = 167.5), 60.5 (CH<sub>2</sub>O, J = 150.7), 20.3 (CH<sub>3</sub>C=O, J = 129.8), 170.1 (C=O); b) in HMPA (expt. 13): n<sub>D</sub><sup>20</sup> 1.4670. <sup>13</sup>C NMR spectrum ( $\delta$ , ppm, J<sub>C-H</sub>, Hz): 124.2 (CCl<sub>2</sub>=), 125.1 (CH=, J = 167.0), 60.33 (CH<sub>2</sub>O, J = 149.9), 20.66 (CH<sub>3</sub>C=O, J = 127.3), 169.6 (C=O). N,N-Dimethylacetamide, n<sub>D</sub><sup>20</sup> = 1.4375, d<sub>4</sub><sup>20</sup> 0.9557. <sup>13</sup>C NMR spectrum ( $\delta$ , ppm, J<sub>C-H</sub>, Hz): 21.08 (CH<sub>3</sub>CO=O, J = 127.3), 34.43 m, 37.48 (CH<sub>3</sub>-N, J = 136), 168.86 (C=O). PMR spectum ( $\delta$ , ppm): 2.3 s (CH<sub>3</sub>C=O), 3.1 s and 3.3 s (CH<sub>3</sub>N).

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