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LETTERS

# Unusual Chlorination of Some Olefins with *Meta*-Chloroperbenzoic Acid in Dichloromethane

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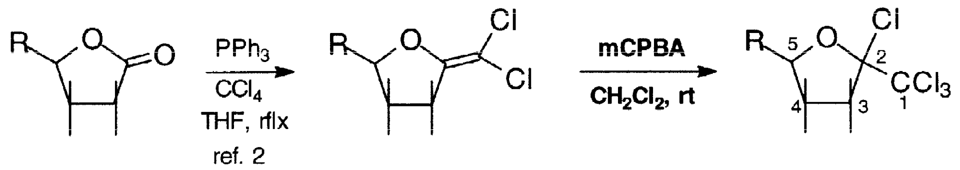
***Abstract*** : In the presence of poorly reactive olefins such as dichloroolefins, *meta-chloroperbenzoic acid reacts with dichloromethane*, probably via a radical mechanism, to produce a powerful chlorinating species which behaves like other chlorinating agents.

We have introduced some years ago the direct olefination of sugar lactones leading to dichloroolefins **II** using tris(dimethylamino)phosphine-tetrachloromethane,[1] and triphenyl-phosphine-tetrachloromethane.[2] One may expect that functionalisation of the anomeric double bond of glycosylidene compounds **II** should lead, with high stereocontrol, to C-glycosidic compounds having a quaternary anomeric centre.[3] Thus we have focused our attention on the transformation of dichloroolefins **II**[4, 5] and we report in this Letter unexpected results from their reaction with *meta*-chloroperbenzoic acid (*m*-CPBA) in dichloromethane.



**I** **II**

In an attempt to prepare anomeric epoxides, dichloroolefin **1** was treated with *meta*-chloroperbenzoic acid (*m*-CPBA) in dichloromethane. In our preliminary experiment a mixture of two products **2** and **3** was formed. If the structure of compound **3** was easily established by spectroscopic analysis which showed clearly the presence of an ester group and of a chlorine atom,[6] the structure of compound **2** was more difficult to establish. $^1$H NMR spectroscopy showed only minor modifications in the chemical shift of H-3 and H-4 (carbohydrate numbering) and the presence of signals at $\delta$ = 76.9 and 77.3 for C-2 and C-1 in $^{13}$C NMR spectrum. Mass spectrometry showed a peak at $m/z$ = 379 $(M - CH_3)^+$ corresponding to a molecular formula $C_{12}H_{15}O_5Cl_4$ and the isotopic pattern of a tetrachloro compound (M, 78.8%; M + 2, 100%; M + 4, 45.5%). It was concluded that $C_{13}H_{18}O_5Cl_4$ was the molecular formula of compound **2**.

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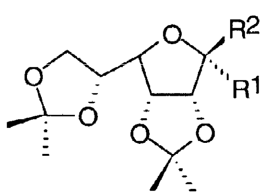
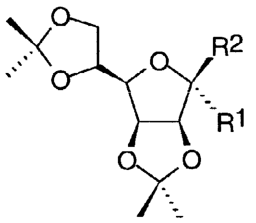
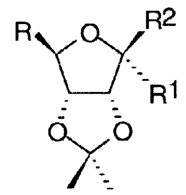
Suspecting that formation of the methylester **3** could be due to the presence of minute amounts of methanol in dichloromethane, we used methanol-free dichloromethane obtained by passage through a column of alumina. Under these conditions the reaction led to the formation of the tetrachloroolefin **2** as the single compound in 65% yield. The next issue was to determine the origin of the chlorine atoms in compound **2.** In order to shed light on this point, we tried different experimental conditions. The replacement of dichloromethane by tetrachloromethane gave only a low yield of **2** (13%). The same observation was made using *para*-nitroperbenzoic acid in dichloromethane. It was concluded that dichloromethane was probably the source of chlorine atoms. To the best of our knowledge, no example of chlorination of double bond using dichloromethane as the source of halogens has been reported. Dichlorination of olefins using hexachloroethane under dibenzoyl peroxide initiation in refluxing toluene was recently reported.[7] However no reaction was observed upon treatment of olefin **1** in dichloromethane in the presence of dibenzoyl peroxide at room temperature.



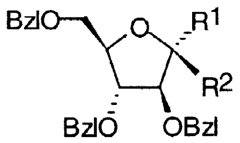
**1** $R^1, R^2 = CCl_2$
**2** $R^1 = Cl$, $R^2 = CCl_3$
**3** $R^1 = Cl$, $R^2 = COOMe$
**4** $R^1 = OH$, $R^2 = CCl_3$



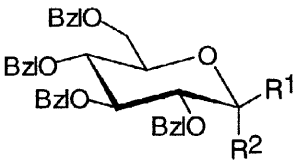
**5** $R^1, R^2 = CCl_2$
**6** $R^1 = CCl_3$, $R^2 = Cl$



**7** $R = H, R^1, R^2 = CCl_2$
**8** $R = H, R^1 = Cl$ $R^2 = CCl_3$
**9** $R = CH_2OAc, R^1, R^2 = CCl_2$
**10** $R = CH_2OAc, R^1, R^2 = CCl_3, Cl$



**11** $R^1, R^2 = CCl_2$
**12** $R^1 = CCl_3$, $R^2 = Cl$



**13** $R^1, R^2 = CCl_2$
**14** $R^1 = CCl_3$, $R^2 = Cl$

Chlorination of several dichloroolefins was attempted with some success as shown in the Table. Good results were obtained with lactones protected with isopropylidene groups (entries 1-4) but the reaction with reagent A (*m*-CPBA-$CH_2Cl_2$) failed with those protected with benzyl groups (entries 5 and 6). This suggested that radicals should be involved in this process, since we have observed that transformations of dichloroolefins involving radical reactions frequently failed when benzyl ethers were used as protecting groups.[4] Indeed total suppression of the chlorination of olefin **1** was observed when the reaction was conducted in the presence of hydroquinone, supporting the intervention of radicals in this reaction. To explain these results, one may suggest that *m*-CPBA could decompose into radicals[8] which should react with dichloromethane to produce chloromethyl and chlorine radicals. The electrophilic chlorine radical can add to the dichloroolefinic bond to form a new radical which should abstract a chlorine to dichloromethane and form chloromethyl radical again. However all attempts to add radicals to dichloroolefins failed so far, showing that dichloroolefins are poor radical acceptors in contrast to the corresponding difluoroolefins.[9] This failure appears to support a partially ionic mechanism for the observed chlorination. To corroborate this hypothesis we examined the reaction of molecular chlorine (reagent B) and triethylammonium trichloride (reagent C)[10] with some dichloroolefins.

**Table.** Chlorination of dichloroolefins using mCPBA-$CH_2Cl_2$

| Entry | Starting olefin | Product | Reagent[a] (Yield %)[b] | | |
|---|---|---|---|---|---|
| 1 | **1** | **2** | **A** (65) | **B** (76) | **C** (90) |
| 2 | **5** | **6** | **A** (59) | **B** (77) | **C** (88) |
| 3 | **7** | **8** | **A** (68) | **B** (88) | c |
| 4 | **9** | **10** | **A** (49) | **B** (73) | c |
| 5 | **11** | **12** | **A** (0) | **B** (86) | c |
| 6 | **13** | **14** | **A** (0) | **B** (76) | **C** (85) |

a) Reagent A: *m*-CPBA (2.5 equiv.) in $CH_2Cl_2$, rt; Reagent B: $Cl_2$ gas, $CH_2Cl_2$, rt, 5 min;
Reagent C: $Et_4N^+$, $(Cl_3)^-$, $CH_2Cl_2$, 0°C, 15 min.

b) Yields refer to pure isolated products

c) Not tested using reagent C

Both reagents B and C react almost instantaneously with dichloroolefins to produce the corresponding tetrachloroolefins in good yields but, interestingly, reagents B and C are efficient in the chlorination of dichloroolefins protected with benzyl groups in contrast to the *m*-CPBA-dichloromethane system, supporting the intervention of radicals in the latter reaction. Whatever the chlorinating reagent used, a single anomer was formed as judged from $^{13}C$ nmr suggesting that the three reagents should operate via the same mechanism. To date, we have been unable to determine the anomeric configuration of the tetrachloro derivatives but it is reasonable to assume that the stereochemical outcome of the reaction is highly controlled by the substituent at C-3. However in the case of the *ribo* derivative **10** (entry 4), both isomers were obtained, probably because both faces of the sugar ring are hindered by the substituent at C-5 and the isopropylidene ring at C-3.

Although, in general, polyhaloolefins are poor substrates in electrophilic reactions,[11] evidence supporting an ionic reaction rather than a radical reaction can be found in our results. For example the formation of chlorohydrine **4** was observed in the reaction of dichloroolefin **1** with chlorine. This side reaction, usually less than 5 %, was found to depend on the dryness of chlorine. Addition of water to the reaction mixture before bubbling chlorine gas through the dichloromethane solution of **1** strongly increased the formation of the chlorohydrine **4**. Thus, chlorination using chlorine and tetraethyl ammonium trichloride is probably an electrophilic attack of chlorine, *trans* with respect to the C-3 substituent.[12] Subsequent opening at C-2 of an intermediate chloronium species by a chloride ion should then occur with inversion of configuration at C-2. However opening of the chloronium intermediate by assistance of the ring oxygen doublet should be possible. The resulting oxonium ion should be attacked by chloride or hydroxide ion *trans* with respect to the C-3 substituent.

In the light of the above results, the reaction of *m*-CPBA in dichloromethane can be explained as follows. Chlorine radical formation from dichloromethane should be initiated by decomposition of *m*-CPBA. As above mentioned dichloroolefins are poor substrates in radical addition, thus chlorine radicals should combine to produce molecular chlorine which then adds immediately to the dichloroolefinic bond, via the ionic mechanism proposed above for the reaction of molecular chlorine.[13] Such chlorination of "standard" olefins in dichloromethane has not been observed previously because *m*-CPBA reacts faster with olefins to form epoxide than it induces decomposition of dichloromethane. Epoxidation of the dichlorovinylether moiety of dichloroolefins is considerably slower, but the oxygen substituent strongly favours electrophilic addition onto this double bond. Moreover it should stabilize an ionic intermediate by formation of an oxonium ion. This unexpected reactivity of dichloroolefins toward electrophilic addition is currently investigated in our group. Under appropriate conditions, the reaction of dichloroolefins with *m*-CPBA in dichloromethane can be directed towards the formation of chloroesters as reported in the accompanying paper.

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