Tetrahedron Letters,Vol.27,No.16,pp 1845-1846,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

STEREOCHEMISTRY OF OXIDATIVE DEIODINATION LEADING TO FORMATION OF COVALENT PERCHLORATES

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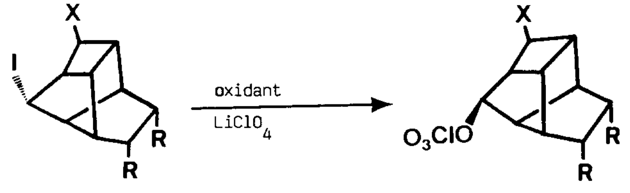
Summary : The oxidative deiodination of several secondary iodides (**1**,**2** and **3**) in the presence of lithium perchlorate proceeds with inversion at carbon to give the corresponding perchlorates. This observation is discussed in terms of the dependence of nucleophilic reactivity of nucleofugic anions on the carbocationic character of transition state of synchronous S_N processes.

Since 1978 we have studied [1] the intriguing phenomenon of competitive binding of nucleofugic anions [2] for a variety of carbocationic-like processes. While its appreciable synthetic potential is out of doubt, we have also emphasized its theoretical importance because this phenomenon leads to a revision of some mechanistic concepts [1].Consider the problem of nucleophilicity of nucleofugic anions [2]. Our data revealed that such anions can successfully compete with usual nucleophiles (e.g. Hal^-, AcO^- etc.) in attack on carbocationic center. Thus,the key question is why these anions can drastically change their "non-nucleophilic" [2] nature?

To explain the observed phenomenon we put forward the hypothesis that "the salts of typical nucleofugic anions,being non-nucleophilic in usual S_N2 reactions, possess the pronounced nucleophilic character either toward transient short-living carbocationic intermediates or for synchronous S_N processes which transition states are resemble to a carbocation" [1]. However,in the course of publication of our papers we often faced with referee comments,which consider this phenomenon in terms of non-selective behavior of high energetic carbocationic intermediates [3].Thus, the cases (i)of stereospecificity and (ii)of high selectivity in favor of nucleofugic anions are significant to shed light on the problem.

Previously we have found that oxidative deiodination of alkyl iodides (eq 1) can proceed quite selectively to give high yields of corresponding perchlorates [4]. The purpose of this paper is to investigate the stereochemical course of the reaction [5]. The cage iodides **1-3** have been chosen as model compounds [6]. We studied the deiodination in the presence of $LiClO_4$ assisted with different oxidants such as Cl_2, NO_2BF_4 and $PhI(OCOCF_3)_2$. The data obtained are summarized in the Table. The reactions proceed quite selectively to give perchlorates **4-7** with high preparative yields.The key result of this study is the total inversion of configuration at the carbon atom independently on an oxidant employed.Perchlorate anion attacks the carbon atom from rear side in respect to a leaving group and these

(1) $R\text{-}I + \text{oxidant} + LiClO_4 \longrightarrow R\text{-}OClO_3$



1-3 **4-8**

1 X=2,4-$(NO_2)_2C_6H_3S$, R=CH_3; **2** X=Br , R=CH_3
3 X=Br,R=$COOCH_3$; **4** X=2,4-$(NO_2)_2C_6H_3SO_2$, R=CH_3
5 X=2,4-$(NO_2)_2C_6H_3SO$, R=CH_3 ; **6** X=Br ; R=CH_3
7 X=Br,R=$COOCH_3$; **8** X=2,4-$(NO_2)_2C_6H_3S$, R=CH_3

reactions exhibit the general stereochemical characteristics of S_N2 process for the fast step of deiodination[7] (eq 2)

$$(2)\ \ {>}C{-}I + Cl_2 \xrightarrow{\text{slow}} [\,{>}C{-}ICl_2\,] \xrightarrow[ClO_4^-]{\text{fast}} [O_3Cl\cdots C\cdots ICl_2]^{\#} \longrightarrow O_3ClO{-}C{<}$$

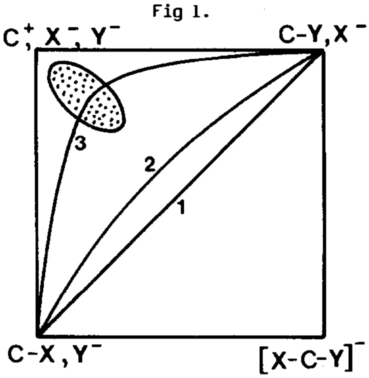
Thus, an intermediate in this reaction exhibits stereospecific behaviour and reacts quite selectively with perchlorate anion. In turn, these data support our aforementioned hypothesis concerning a nucleophilicity of nucleofugic anions. Clear visualization can be made using More O'Ferrall diagramm[8] (Fig 1). Our assumption means that the apparent nucleophilicity of nucleofugic anions are extremely dependent on carbocationic character of transition state. These anions can play two roles either being non-nucleophilic species in "neutral" (line 1, Fig 1) S_N2 reactions (or even in S_N2 with "modest S_N1 character"; line 2, Fig 1), or being powerful and competitive nucleophiles in the reactions with pronounced S_N1 character ("ion-sandwich like", "open" transition state; line 3, Fig 1).

Table. Oxidative deiodination of **1-3** in the presence of lithium perchlorate [6d].

iodide	oxidant (mol-eqv)		temp C°	h	products (yields %)
1	$PhI(OCOCF_3)_2$	(2)	20	1	**4**(61), **5**(21)
2	$PhI(OCOCF_3)_2$	(1)	20	1	**6**(85)
2	Cl_2	(3)	0	0.1	**6**(81)[&]
2	NO_2BF_4	(2)	0	1	**6**(95)
3	NO_2BF_4	(2)	20	3	**7**(86)

[&] Chlorides (<10%) were also identified in the mixture by NMR.

Fig 1.



Dotted area - region of sharply increased nucleophilisity of nucleofugic anions.

REFERENCES AND NOTES

1 N.S.Zefirov and A.S.Koz'min, Acc.Chem.Res., **18**, 154(1985).

2 We conventionally accept as "nucleofugic anions" those which play usually role of a leaving group while their nucleophilic properties can be ignored. ClO_4^-, FSO_3^-, $CF_3SO_3^-$ and even TsO^- fall into this definition. In fact, the supernucleofugic anions such as ClO_4^- are often considered in literature as "non-nucleophilic" anions.

3 We would like to present one of the referee comments: " It has become quite clear from recent work by Rappoport and by Jencks that ordinary alkyl cations, even benzylic and allylic ones, are so reactive, that they react almost totally non-selective. Product ratio obtained from such species give no information about nucleophilicities..."

4 N.S.Zefirov, V.V.Zhdankin, G.V.Makhon'kova, Yu.V.Dan'kov and A.S.Koz'min, J.Org.Chem., **50**, 1872(1985).

5 (a) Deiodination of trans-2-chlorocyclohexyl iodide proceeds with complete retention to give trans-products exclusively[5b]. However, this fact can not be generalized because the cyclohexyl system employed has an inherent bias for a neighbouring group assisted pathway leading virtually to retention of configuration. (b) R.C.Cambie, D. Chambers, B.G.Lindsay, P.S.Ruthledge and P.D.Woodgate, J.Chem.Soc.Perkin I, **1980**, 822.

6 (a) The covalent perchlorates of this cage system are sufficiently stable and some of them (**6-8**) have been used as a model to demonstrate the inversion at carbon in S_N reactions in acetone with a variety of nucleophiles[6b]. The iodides **1-3** were obtained from the corresponding perchlorates **6-8** by the treatment with NaI in acetone (90-95%) and purified by cristallisation. (b) N.S.Zefirov, A.S.Koz'min and V.V.Zhdankin, Dokl.Akad.Nauk SSSR, **262**, 104(1982). (c) Rigorous NMR stereochemical characterization is based on the following criteria (Ref.6b): H-6 for anti-configuration (type **4-8**) gives a narrow singlet, but for syn-configuration (type **1-3**) the signal is dd with J 8Hz and 3 Hz. (d) All reactions were performed in AcOEt in the presence of 5 mol-eqv of lithium perchlorate. Preparative yields after a purification either by chromatography or by cristallisation are presented. Tlc and NMR indicates exclusively the presence of the products, indicated in Table with the lack of epimeric materials. A satisfactory elemental analysis was obtained for all new compounds.

7 (a) Kinetics of the oxidative deiodination evidence that the slow step of the process is the oxidation of the iodine into transient species having iodine in I^{+3} state[7b]. Thus, term S_N2 must be applied to the fast product determined step of this multistep reaction. (b) K.B.Wiberg, W.E.Pratt and M.G.Matturo, J.Org.Chem., **47**, 2720(1982).

8 See J.M.Harris, S.G.Shafer, J.R.Moffatt and A.R.Becker, J.Am.Chem.Soc., **101**, 3295(1979); J.R.Murdoch, Ibid., **105**, 2660 (1983) and references therein.

(Received in UK 12 February 1986)