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Hypervalent Iodine Induced Nucleophilic Additions to Alkenes : Synthesis of 1,2-Diperchlorates.

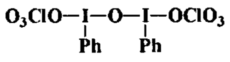
Antonella De Mico[a], Roberto Margarita[b], Luca Parlanti[b], Giovanni Piancatelli[*b] and Andrea Vescovi[b].

Centro CNR di Studio per la Chimica delle Sostanze Organiche Naturali [a] and Dipartimento di Chimica[b], Università "La Sapienza", P.le Aldo Moro 5, 00185 Roma, Italy
E-mail : piancatelli@axrma.uniroma1.it.

Abstract : a novel iodine (III) reagent has been developed by the BAIB/$Mg(ClO_4)_2$ reagent combination. Reaction of this reagent with alkenes yielded 1,2-diperchlorates. © 1997 Elsevier Science Ltd.

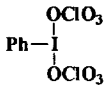
In recent past years, there has been increasing interest in derivatives of the hypervalent iodine (III) reagents. This is due to the wide utility of such compounds in synthetic organic chemistry. In addition, their reactions represent one of the most attractive and environmentally less-hazardous procedures.[1]

A few years ago, Caple and Zefirov [2] developed a series of novel iodine (III) reagents. Particularly the authors described the preparation of μ-oxodiiodo-diphenyl diperchlorate **1** obtained by reaction of [bis(acetoxy)iodo]benzene (BAIB) with aqueous perchloric acid (Figure 1).



$$O_3ClO-\underset{Ph}{I}-O-\underset{Ph}{I}-OClO_3$$

1



$$Ph-\overset{OClO_3}{\underset{OClO_3}{I}}$$

2

Figure 1

However, the only reported application was the formation of *cis* 1,2-diperchlorate cyclohexane, by reaction of **1** with cyclohexene.[2]

Its synthetic utility has not been exploited fully to date. There are no further studies about the chemical reactivity of reagents such as **1** with alkenes.

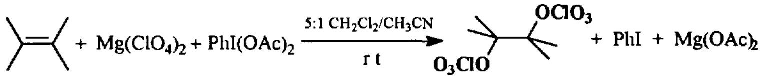
More recent works pointed out the capability of the reagent combination of BAIB and salts, such as $Mg(ClO_4)_2$,, to promote the efficiency of reactions involving radical species, increasing both reaction rates and yields.[3] During our studies on the chemistry of the hypervalent iodine (III) reagents,[4] we discovered that BAIB was able to react immediately with $Mg(ClO_4)_2$ in ethyl acetate, giving a yellow crystalline compound,

[bis(perchlorate)iodo]benzene 2, never described before (Figure 1, Scheme 1). Other salts, such as lithium, barium , sodium and tetrabutyl ammonium perchlorates did not give rise to the formation of 2 by reaction with BAIB.

$$PhI(OAc)_2 + Mg(ClO_4)_2 \xrightarrow[r\,t]{CH_3CO_2Et} \underset{\mathbf{2}}{PhI(ClO_4)_2} + Mg(OAc)_2$$

Scheme 1

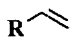
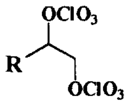
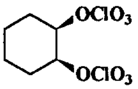
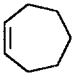
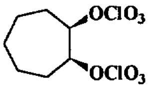
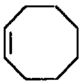
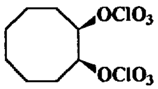
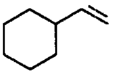
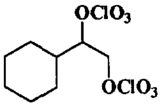
In the present paper, we wish to report the utility of the novel reagent, which can effect the 1,2-functionalisation of alkenes, giving 1,2-diperchlorates.



Scheme 2

In running experiments, the reagent **2** was prepared *in situ* , by mixing BAIB and $Mg(ClO_4)_2$ in a (5:1) CH_2Cl_2/CH_3CN mixture. The addition of alkenes provided 1,2-diperchlorates (Scheme 2, Table1).

Table 1. Reaction of alkenes with $BAIB/Mg(ClO_4)_2$

Entry	Substrate	Product	Time h	Yield %
1	 $R = C_nH_{2n+1}$ n = 4-8		3-4	50-60
5			4	50
6			4	50
7			4	40
8			3	60

The nucleophilic addition has proven to be particularly successful with terminal alkenes. Even more, the synthetic utility appears important with symmetrical cyclic alkenes (entries **5**, **6**, **7**) where the addition is stereospecific.

The reaction on more substituted alkenes, such as methylcyclohexene, led to a formation of unstable compounds, never isolated.

Electron poor systems were recovered unreacted from the reaction medium, meanwhile electron rich ones, such as dihydropyran and styrenes reacted immediately, providing very unstable and non-isolable compounds.

Due to the instability of 1,2-diperchlorate compounds, all the yields of chromatographically homogeneous materials are lower than those obtained by GC analysis .

The best results were obtained utilising $Mg(ClO_4)_2$ as added salt to the reaction medium. Other salts such as $LiClO_4$, $Ba(ClO_4)_2$, $NaClO_4$ and $(Bu_4N)ClO_4$ gave either lower yields (Table 2, entries **2** and **3**) or no reaction products (Table 2, entries **4** and **5**).

Table 2. Reaction of 1-decene with BAIB and perchlorate salts.

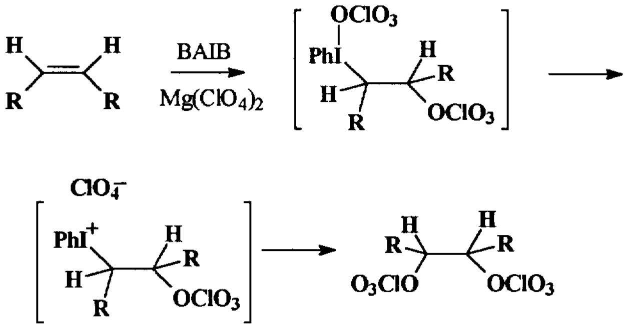
Entry	Perchlorate salt	Time h	Yield % by
1	$Mg(ClO_4)_2$	4	80
2	$Ba(ClO_4)_2$	4	30
3	$LiClO_4$	4	60
4	$NaClO_4$	4	-
5	$(Bu_4N)ClO_4$	4	-

These results can be explained by a combination of two factors, the solubility of the added salts in the reaction medium and the stability of the metal acetates, which are formed during the reaction with BAIB (Scheme 1).

In fact, we found that $Ba(ClO_4)_2$ and $NaClO_4$ were not soluble under our experimental conditions. $(Bu_4N)ClO_4$ was completely soluble, while $Mg(ClO_4)_2$ and $LiClO_4$ could be partly dissolved.

Even more, the stability of the metal acetates (Scheme 2) are decreasing, as shown: $Ba(OAc)_2 \sim Mg(OAc)_2 > NaOAc > LiOAc > (Bu_4N)OAc$.[5]

It is worth noting that the absence of nucleophilic ligands at the iodine atom (perchlorate anion is a very weak nucleophilic ligand) makes the reagent **2** very reactive, with a high electrophilic character. Following this statement, the reaction pathway can be explained by referring to the mechanism described for the hypervalent iodine (III) reagents by Moriarty *et al.*[6] The initial electrophilic addition of the reagent **2** to alkenes could give rise to the formation of an intermediate, such as a (Scheme 3). Then, the displacement of iodobenzene by the perchlorate anion leads to the 1,2-diperchlorates. The stereochemical outcome observed with cyclic alkenes is completely in agreement with the proposed mechanism, which leads to the formation of *cis* rather than *trans*-addition products.



Scheme 3

In conclusion, we have demonstrated the utility of the new reagent **2** for the formation of 1,2-diperchlorates. The reactions were efficient both with terminal and symmetrically disubstituted cyclic alkenes. Due to the great mobility of the perchlorate anion as leaving group, the described compounds are synthetically useful for further manipulations.

Experimental.

General Experimental. ^1H (200 MHz) and ^{13}C (50MHz) nuclear magnetic resonance spectra were recorded at room temperature in $CDCl_3$ solution. Mass spectra were obtained on a mass spectrometer using HPLC-MS coupling. Flash chromatography was executed with Merck Kieselgel 60 (230-400 mesh) using mixture ethyl acetate/hexane as eluants. All commercially available reagents were purchased from Aldrich and purified before use by distillation on Na.

General Procedure for the synthesis of 1,2-diperchlorates: $Mg(ClO_4)_2$ (1 mmol) and BAIB (1 mmol) were added under stirring to (5:1) CH_2Cl_2/CH_3CN (6 ml) at room temperature. Substrate (1 mmol) was then added after 15 min. When the oxidant has totally reacted, the reaction mixture was diluted with ethyl acetate and washed with aqueous $Na_2S_2O_3$. The aqueous phase was then extracted with ethyl acetate and the organic layer was washed with brine and dried on Na_2SO_4. The crude product obtained after vacuum evaporation was purified by column flash chromatography. All pure products were characterised by ^1H- and ^{13}C-NMR spectroscopy.

Caution ! Neat 1,2-diperchlorates can explode violently on contact or heating. Due to detonation and decomposition of neat products, exact mass determination and elementary analysis couldn't be performed.

1,2-Diperchlorate *n*-hexane : viscous oil, ^{1}H-NMR (δ, CDCl3) : 5.05-5.15 (1H, m) ; 4.62 (1 H, dd, J_1=6 Hz, J_2=6 Hz); 4.17 (1 H, dd J_1=10 Hz, J_2=4 Hz); 1.7-1.9 (2 H, m); 1.2-1.5 (4 H, m); 0.9 (3H, t). ^{13}C-NMR (δ, $CDCl_3$) : 83.18; 72.8; 30.25; 27.78; 22.67; 14.04.

1,2-Diperchlorate *n*-heptane : viscous oil, ^{1}H-NMR (δ, CDCl3) : 5.0-5.1 (1H, m) ; 4.62 (1 H, dd, J_1=6 Hz, J_2=6 Hz); 4.2 (1 H, dd J_1=10 Hz, J_2=4 Hz); 1.7-1.95 (2 H, m); 1.2-1.5 (6 H, m); 0.9 (3H, t). ^{13}C-NMR (δ, $CDCl_3$) : 83.45; 72.88; 30.14; 29.90; 25.72; 22.75; 14.08.

1,2-Diperchlorate *n*-octane : viscous oil, ^{1}H-NMR (δ, CDCl3) : 5.05-5.15 (1H, m) ; 4.61 (1 H, dd, J_1=6 Hz, J_2=6 Hz); 4.2 (1 H, dd J_1=10 Hz, J_2=4 Hz); 1.7-1.95 (2 H, m); 1.1-1.5 (8 H, m); 0.9 (3H, t). ^{13}C-NMR (δ, $CDCl_3$) : 83.7; 72.93; 32.04; 29.65; 25.69; 25.37; 22.76; 14.07.

1,2-Diperchlorate *n*-decane : viscous oil, ^{1}H-NMR (δ, CDCl3) : 5.05-5.15 (1H, m) ; 4.63 (1 H, dd, J_1=6 Hz, J_2=6 Hz); 4.20 (1 H, dd J_1=10 Hz, J_2=4 Hz); 1.7-1.9 (2 H, m); 1.0-1.5 (10 H, m); 0.9 (3H, t). ^{13}C-NMR (δ, $CDCl_3$) : 84.07; 73.28; 31.9; 30.33; 29.32; 29.24; 29.10; 24.68; 22.77; 14.16.

***cis*-1,2-Diperchlorate cyclohexane** : viscous oil, ^{1}H-NMR (δ, CDCl3) : 5.15 (2 H, m, W=12 Hz) [2] ; 2.0-2.2 (2 H, m); 1.75-1.95 (4 H, m); 1.4-1.6 (2 H, m). ^{13}C-NMR (δ, $CDCl_3$) : 83.64, 66.31; 27.93; 21.04; 15.39.

***cis*-1,2-Diperchlorate cycloheptane** : viscous oil, ^{1}H-NMR (δ, CDCl3) : 5.15 (2 H, m, W=12 Hz) [2] ; 2.1-2.4 (2 H, m); 1.95-2.1 (2 H, m); 1.5-1.9 (6 H, m). ^{13}C-NMR (δ, $CDCl_3$) : 82.46; 28.49; 28.19; 23.62.

***cis*-1,2-Diperchlorate cyclooctane** : viscous oil, ^{1}H-NMR (δ, CDCl3) : 5.15 (2 H, m, W=12 Hz) [2] ; 2.0-2.3 (2 H, m); 1.9-2.1 (2 H, m); 1.4-1.9 (8 H, m).

2-Cyclohexyl-1,2-diperchlorate ethane: viscous oil, ^{1}H-NMR (δ, CDCl3) : 4.8-4.9 (2 H, m); 4.69 (1 H, q, J=3 Hz); 1.6-2.0 (6 H, m); 1.0-1.4 (5 H, m). ^{13}C-NMR (δ, $CDCl_3$) : 78.2; 70.16; 33.03; 30.37; 26.24; 21.40.

Synthesis of [bis(perchlorate)iodo]benzene (BPIB) (yellow crystalline solid) : 2 mmol of both $Mg(ClO_4)_2$ and BAIB were added to stirred ethyl acetate (10 ml). A yellow solid fine precipitate (BPIB) was obtained after 30 minutes. Ethyl acetate was then removed by decantation. Pure BPIB was then obtained by filtering the yellow solid and washing with ethyl acetate. Pure [bis(perchlorate)iodo]benzene can be stored at room temperature for weeks without particular caution. Due to detonation and decomposition of BPIB occurring around 100 °C, elemental analysis couldn't be performed. Nevertheless IR, HPLC-MS, ^{1}H- and ^{13}C-NMR spectra of BPIB allowed the comprehension of the structure **2**.

^{1}H-NMR (δ, CDCl3) : 8.30-8.34 (1 H, m) ; 7.72-7.75 (2 H, m) ; 7.47-7.49 (1 H, m) ; 7.26-7.31 (1 H, m). ^{13}C-NMR (δ, $CDCl_3$) : 137.39 ; 134.45 ; 132.442 ; 131.32 ; 130.96 ; 128.0. IR (cm^{-1}, nujol mull) : 1200 (broad) ; 1150 (broad) ; 1100 (sharp) ; 730 (sharp) ; 680 (sharp) ; 620 (sharp) ; 560 (broad) ; 420 (broad) ; 355 (broad). HPLC-MS (CH_3CN) m/e: 403 (M^+); 303 (M- ClO_4) ; 204 (PhI).

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