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NOVEL REAGENTS CONTAINING HYPERVALENT IODINE AND THEIR USE FOR ELECTROPHILIC ADDITIONS TO OLEFINS

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SUMMARY: A series of novel I(III) containing reagents have been developed and their electrophilic reactions with olefins giving *vic*-disubstituted derivatives (including *vic*-ditriflates) are described.

There has been considerable interest in I(III) containing compounds as reagents in organic synthesis[1]. In particular, iodobenzene diacetate and iodobenzene bis-(trifluoroacetate) have become useful reagents[1], especially for the oxidation of organic compounds[2]. Our interest in these compounds stemmed from our recent discovery of the intriguing phenomenon of competitive binding of nucleofugic anions (including ClO_4^-, FSO_3^-, $CF_3SO_3^-$ and TsO^-) in carbocationic-like processes[3] which, in addition to extensive synthetic applications, is no doubt of theoretical importance. Along this line, we were particularly interested by a report that iodobenzene hydroxytosylate (2*a*) effects the *cis-1,2*-ditosylation of olefins[4]. In an attempt to develop reagents which would effect the transformation of olefins into synthetically valuable *vic*-derivatives, we have created a series of novel I(III) containing reagents capable of acting as electrophiles.

In the present paper we wish to report *(i)* the development of *the novel reagents (1c, 2b,c, 3-5, 7)* which can effect the *1,2*-functionalization of olefins and *(ii)* the application of the known I(III) containing reagents *in combination with an added salt* (which acts as a source of an external nucleophile) to give *vic*-derivatives, *including 1,2-diperchlorates* and *1,2-ditriflates*.

The reagents used[5] are given by formulas *(1-7)*. General schemes of their reactions with olefins are represented by equations *1, 2,* and *3.* The reaction conditions and the yields of the products are summarized in *Table 1.* The yields refer to the isolated, chromatographically and spectroscopically homogeneous materials. Satisfactory elemental analysis data were obtained for all new compounds.

The main results of this paper may be summarized as follows. First of all, equations *1* and *3* clearly demonstrate that the I(III) containing reagents investigated are able to add to a double bond with incorporation of both an internal an external nucleophile (from the added salt) and with subsequent substitution of the iodine framework in

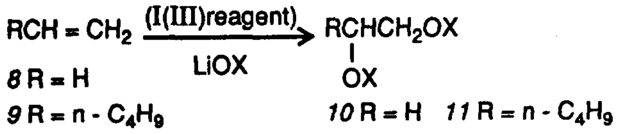
TABLE 1
REACTIONS OF REAGENTS 1-7 WITH OLEFINS 8, 9, AND 14

Reagent	Olefin	Salt (mol-eqv)	Temp °C	Time h	Product	% Yield
1b	*9*	LiOTf (5)	25	10	*11d*	(10)
1b	*9*	$LiClO_4$(5)	25	10	*11c*	(20)
1c	*9*	-	25	0.5	*11b*	(68)
1c	*14*	-	0	1	*16a*	(99)
2a	*9*	LiOTf (5)	25	10	*11d*	(15)
2a	*14*	$LiClO_4$(5)	25	8	*15a*	(30)
2b	*9*	-	20	5	*11e*	(60)
2c[b]	*8*	-	60	1	*10a*	(30)
2c	*14*	-	0	0.8	*16b*	(8)
					16c	(60)[c]
3a	*9*	-	25	5	*11c*	(45)
3a	*14*	-	0	0.5	*15a*	(60)
3b	*9*	-	25	7	*11d*	(35)
3b	*14*	-	0	0.5	*15b*	(50)
4	*9*	-	25	5	*13*	(80)
5	*8*	-	15	0.3	*12*	(85)
5	*9*	-	10	0.2	*13*	(70)
6	*9*	$LiClO_4$(2)	0	0.1	*11c*	(70)
6	*14*	Bu_4NOTs(2)	0	0.5	*15c*	(55)
7	*14*	Bu_4NOTs(2)	0	0.5	*15c*	(50)

a The reactions of *1b* and *2a* were made in AcOEt; the others were made in CH_2Cl_2.

b The reaction was performed in CH_3NO_2.

c The compound *16b* decomposes during chromatography on silica get to give *16c.*

[1] 

$$RCH=CH_2 \xrightarrow[\text{LiOX}]{\text{(I(III)reagent)}} \underset{\displaystyle OX}{RCHCH_2OX}$$

8 R = H

9 R = n - C_4H_9

10 R = H *11* R = n - C_4H_9

a X = Ts *b* X = CF_3CO

c X = ClO_3 *d* X = CF_3SO_2

e X = CH_3SO_2

an intermediate by a nucleophile to give *1,2-vic*-derivatives. A plausible mechanism[4] is expressed by equation *4*. This mechanism accounts for the formation of *cis*-addition products (e.g. *15a*).

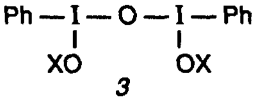
Secondly, the nucleofugic anions such as ClO_4^- and TfO^- can play the role of nucleophilic species in the course of these reactions. Moreover, the incorporation of these anions from the added salts is another manifestation of the general phenomenon of the competitive binding of nucleofugic anions in carbocationic-like processes[5]. It is significant to note that the formation of *1,2*-diperchlorates and *1,2*-ditriflates reveals the nucleophilic character of these anions for the process of S_N2 substitution with inversion at carbon (equation *4*, step *B*). The mechanistic significance of such processes recently has been discussed[6]. Thirdly, the novel reagents *4* and *5* offer a versatile means to effect a direct transformation of olefins into their cyclic sulfates (equation *2*). In principle, the reagent *5* can be considered as a *1,4*-dipole which can react with olefins *via* intermediate formation of derivatives of iododioxathiane[7].

$R-I(OX)_2$

1

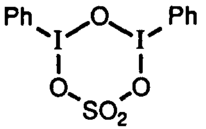
$R-I(OH)OX$

2



$Ph-I(OX)-O-I(OX)-Ph$

3



4

$Ph-\overset{+}{I}-OSO_2\overset{-}{O}$

5

$Ph-\overset{+}{I}-O\cdot\overset{-}{BF_3}$

6

$Ph-\overset{+}{I}-ONO_2\cdot\overset{-}{BF_4}$

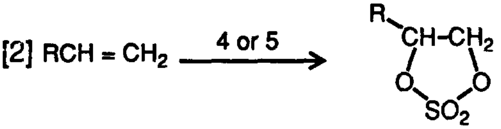
7

Where

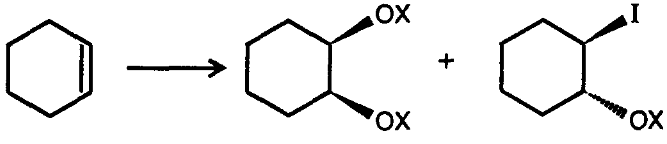
In *1* *a* $R = Ph$ $X = COCH_3$
b $R = Ph$ $X = COCF_3$
c $R = C_3H_7$ $X = COCF_3$

In *2* *a* $R = Ph$ $X = Ts$
b $R = Ph$ $X = Ms$
c $R = C_3F_7$ $X = Ts$

In *3* *a* $X = ClO_3$
b $X = CF_3SO_2$

[2] 

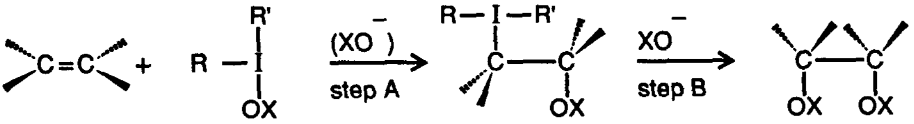
12 $R = H$ *13* $R = n-C_4H_9$

[3] 

14 *15* *16*

15
a $X = ClO_3$
b $X = CF_3SO_2$
c $X = Ts$

16
a $X = CF_3CO$
b $X = Ts$
c $X = H$

[4] 

Finally, it is worthy to emphasize the preparative value of the investigated reactions which open a route to new types of *1,2-vic*-derivatives from olefins.

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5. (a) Literature procedures were used for the preparation of the reagents *1c*[5b], *2a*[4], *6*[5c]. Mesylate *2b* was obtained by treatment of *1a* with methanesulfonic acid in $CHCl_3$ (m.p. 119–120°, 81% yield). Tosylate *2c* was obtained by heating equimolar amounts of *1c* and *p*-TsOH·H_2O in CH_2Cl_2 (m.p. 124–125°, 73% yield). μ-Oxodiiodo-(III)diphenyldiperchlorate, *3a* was obtained from *1a* and perchloric acid (temp. of dec. 116–118°, 85% yield). Ditriflate *3b* was obtained analogously by treatment of *1a* with triflic acid in $CHCl_3$ (m.p. 119–121°, 73% yield). Reagent *7* was obtained from $(PhI{=}O)_n$ and NO_2BF_4 in CH_2Cl_2 at −20° (unstable at room temperature). For an elaboration of the characterization of reagents of this type, see the review by Zefirov and Koz'min and references cited therein[3b]. The sulfates *4* and *5* were obtained by the interaction of $(PhIO)_n$ with either one-half or one equivalent, respectively, of SO_3 in CH_2Cl_2 at −78°. Reagent *4*, which could be subsequently converted to reagent *5*, was isolated as a moisture sensitive powder (temp of dec. 108–110°) and was characterized by IR and NMR (e.g., *C–I*, 460 cm^{-1} and *I–O*, 560 cm^{-1}). Reagent *5*, formed either directly from $(PhIO)_n$ or *4*, likewise was isolated in a similar form (temp of dec. 76–70°) and also exhibited anticipated IR and NMR characteristics (*C–I*, 465 cm^{-1} and *I–O*, 560 cm^{-1}. (b) V.V. Lyalin, V.V. Orda, L.A. Alexeeva, L.M. Yagopul'sky, *Zh. Org. Khim., 1970, 6*, 329. (c) M. Ochial, E. Fujita, M. Arimoto, H. Yamaguchi, *J. Chem. Soc., Chem. Comm., 1982*, 1108.

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7. (a) [2+2+2] Cycloaddition of SO_3 with double or triple bonds of different types is known. Indeed, the formation of *4* also falls into this category. (b) The ylide $PhI{=}C(COOCH_3)_2$ also reacts with SO_3 (CH_2Cl_2, room temperature) to give methyl *2,2,5,5*-tetraoxo-*1,4*-dioxa-*2,5*-dithiane-*3,3,6,6*-tetracarboxylate, the structure of which was proven by X-ray analysis (K.A. Potekhin, Yu. T. Struchkov, V.D. Sorokin, V.V. Zhdankin, A.S. Koz'min, N.S. Zefirov, *Dokl. Akad. Nauk SSSR, in press*).

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