Oxidative Cleavage and Rearrangement of Aryl Epoxides Using Iodosylbenzene: on *Criegee*'s Trail

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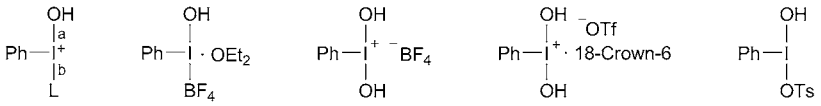
To *D. S.* – with admiration and gratitude

Aryl epoxides undergo rearrangement and oxidative cleavage when reacted with *in situ* prepared hydroxy-λ^3-iodane complexes. The presence of H_2O plays a decisive role in steering the reaction path. A mechanistic scheme is proposed that accounts for the observed chemoselectivities.

Introduction. – Iodosylbenzene (PhIO) is a pale-yellow amorphous powder, and practically insoluble in inert solvents. Iodosylbenzene reacts with several reagents to form unstable hydroxy-λ^3-iodane complexes. They decompose with different half-lives resulting in black tar and/or PhI. The decomposition rate is highly dependent on the bond lengths '*a*' and '*b*' (*Fig.*) [1–3].



1 **2** **3** **4**

Figure. *Hydroxy-λ^3-iodane complexes*

Oxidative C–O and C–C cleavage reactions of epoxides with various oxidizing agents have long been established and are used widely in industrial processes. Some of the commercial reagents in use for this purpose are: $NaIO_4$ [4], HIO_4 [5], $LiClO_4$ [6], or oxo-metal compounds in high oxidation states: $RuCl_3/K_2SO_5$ [7], OsO_4 [8], WO_3/H_2O_2 [9], *etc.* The stereo-, regio-, and enantioselective aspects of the oxidative cleavage of epoxides were widely studied, too [10].

Hypervalent iodine reagents have been in use for oxidation, rearrangement, and fragmentation reactions of organic substrates. Historically, the first application of a hypervalent iodine reagents for the oxidative cleavage of 1,2-diols was developed by *Criegee* and *Beuker*. They showed that 1,2-diols react with (diacetoxyiodo)benzene and AcOH in benzene to yield the corresponding aldehydes [11]. Later, *Chen et al.* found that 1,2-diols undergo the same reaction with (polystyrene)–$I(OAc)_2$ in CH_2Cl_2 at room temperature. Protecting groups such as AcO, RO, BnO, BzO, and acetonides do not react under these reaction conditions [12]. The oxidative cleavage of olefins to the corresponding carbonyl compounds using complex **3** [2a] and the rearrangement of

olefins to the corresponding aldehyde using [hydroxy(tosyloxy)iodo]benzene (**4**; commonly referred to as the *Koser* reagent) were also described [13].

Results and Discussion. – Derivatives of (diacetoxyiodo)benzene such as *I*,*I*-bis(trifluoracetoxy)iodobenzene were already employed for the reaction with epoxides by *Spyroudis* and *Varvoglis* [14]. They demonstrated for the first time that addition of *I*,*I*-bis(trifluoracetoxy)iodobenzene led to oxidative C–O and C–C cleavage and/or rearrangement reactions. However, the yield of the products was just moderate-to-fair, and it turned out that the different reaction pathways were difficult to control.

Here, we describe the oxidative cleavage and rearrangement reactions of alkyl- and/or aryl-substituted substrates using PhIO and HBF_4 (in H_2O or in Et_2O; *Table 1*). We found that, by using PhIO, C–C cleavage or a rearrangement reaction can be selectively achieved by setting the reaction conditions. Independent from the nature of the substrate, the C–C cleavage reaction of epoxides in the presence of H_2O is faster compared to the rearrangement reaction (*Entries 5* and *6*, and *Entries 9* and *10*, *Table 1*). When the substituents have a low migratory aptitude (*e.g.*, Me group; *Entries 4–6*), the reaction proceeds *via* C–C oxidative cleavage, even when no H_2O is present. The rearrangement reaction proceeds when the substrate has substituent(s) with a reasonable migratory aptitude (*e.g.*, H or aryl group) under anhydrous reaction conditions (*Entries 8* and *10*, *Table 1*).

We assume that the C–C cleavage reaction of epoxides is catalyzed by H_2O added to or formed during the reaction. The pathway to the rearranged products can be chosen by setting anhydrous reaction conditions (molecular sieves (4 Å), $HBF_4 \cdot OEt_2$ 50–55% in Et_2O; *Entries 8* and *10*, *Table 1*). The results compiled in *Tables 2* and *3* (substrates *trans*-stilbene oxide and styrene oxide, resp.) show that the yields of rearranged and oxidative C–C cleavage products are strongly dependent on the reaction conditions. The yields of PhCHO under anhydrous reaction conditions (using molecular sieves (4 Å) are much lower compared to conditions without molecular sieves (*Entries 1–4*, *Table 2*). The C–C cleavage product is the major product if aqueous HBF_4 (48% in H_2O) is the reagent (*Entry 7*, *Table 2*).

Whether styrene oxide reacts under oxidative C–C cleavage or H rearrangement to PhCHO cannot be deduced from the substrates listed in *Table 3* (*Entries 1* and *2*). Thus, we decided to conduct the reaction with the ^{2}H-substituted analog *rac*-(β,β-$^2H_2$)styrene oxide as substrate (*Scheme 1*). Under H_2O-free conditions (using molecular sieves (4 Å), the ratio PhC(O)^{2}H (rearrangement product)/PhC(O)H (product of C–C cleavage) turned out to be 2 : 1. Bearing in mind that ^{2}H-rearrangement is discriminated against H rearrangement by a kinetic isotope effect, and that neither the degree of deuteration of the substrate nor exclusion of H_2O will be 100% complete, it is safe to declare that styrene oxide reacts predominantly under rearrangement.

In the light of these results and precedence for reactions using similar reagents [14], we propose the reaction mechanism outlined in *Scheme 2*[1]). Complex **1**, prepared *in*

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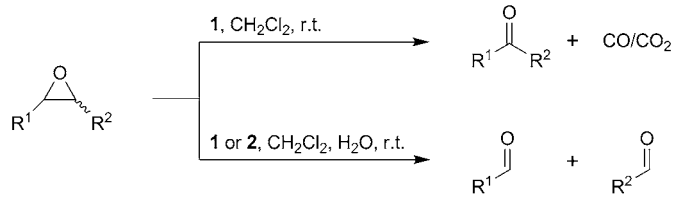
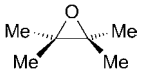
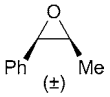
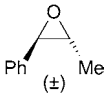
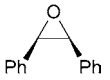
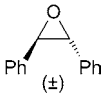
[1]) Further corroboration for this mechanistic scheme comes from an experiment with *rac*-(β,β-$^2H_2$)styrene oxide in the absence of molecular sieves (4 Å). Because of the H_2O formed during the reaction, C–C cleavage becomes the dominant reaction leading to undeuterated PhCHO as the major product.

Table 1. *Oxidative Rearrangement and C–C Cleavage of Epoxides*

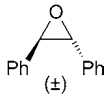


Entry	Substrate	Reagent	HBF_4 Drop rate [ml/h]	CH_2Cl_2 [ml]	Time [h]	Product(s)	Yield [%]
1		**1**	1	20	3	no reaction	
2		**2**	–	30	4	PhCHO	65
3[a])		**1**	3.5	50	7	PhCHO	54
4[c])		**1**	2	12	1	PhCHO	16
5[b])[c])		**1**	5	20	3.5	PhCHO	62
6[a])[c])		**2**	–	10	24	PhCHO	86
7		**1**	2.5	20	4	MeC(O)Ph	60
8		**1**	5	20	3.5	Ph_2CO, PhCHO	51, 3
9		**2**	–	20	1	PhCHO, Ph_2CO	64, 24
10		**1**	3	30	3	Ph_2CO, PhCHO	71, 27

[a]) The yield was determined by GC analysis with 1,4-dichlorobenzene or mesitylene as internal standards. [b]) The reaction was carried out at $-40°$. [c]) Formation of MeCHO was not observed.

situ from PhIO and $HBF_4 \cdot OEt_2$ (50–55% in Et_2O), is first attacked by the epoxide substrate to form the epoxide-λ^3-iodane **5**, which is in equilibrium with the open-chain carbocation **6**. In the presence of H_2O, the carbocation reacts to intermediate **7** which then under C–C cleavage yields the corresponding carbonyl compounds, PhI, and H_2O. However, under anhydrous reaction conditions, the reaction proceeds under rearrangement of the R′ substituent (R′ = H, aryl) to the intermediate **8** which, under proton loss, gives rise to intermediates **9** and **10**. The formation of a cyclic intermediate similar to **10** was postulated earlier in [15]. The cyclic intermediate then undergoes cleavage in a concerted fashion to the carbonyl product, HCHO, and PhI. Formaldehyde is short-lived and could not be detected by ^{1}H-NMR spectroscopy in our experiments. We assume that HCHO is first oxidized to HCOOH, and further to CO

Table 2. *Oxidative C–C Cleavage and Rearrangement Reaction of* rac-trans-*Stilbene Oxide*



Entry	Reagent	CH_2Cl_2 [ml]	HBF_4 Drop rate [ml/h]	Time	Conversion [%]	Yield [%][a])	
						Ph_2CO	PhCHO
1	**1**	40	3	7 h	100	36	13
2	**1**	100	6	8 h	57	46	11
3	**1**	100	7.2	7 h	84	46	14
4	**1**	30	3	3 h	100	71	13
5[b])	**1**	30	–	10 min	100	44	6
6[b])	**1**	30	3	3 h	95	50	2
7	**2**	30	–	10 min	100	24	64

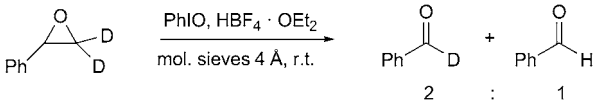
[a]) Yields were determined by GC analysis with mesitylene as internal standart. [b]) With molecular sieves (4 Å).

Table 3. *Oxidative C–C Cleavage and Rearrangement Reaction of* rac-*Styrene Oxide*

Entry	Reagent	CH_2Cl_2 [ml]	HBF_4 Drop rate [ml/h]	Time [h]	Conversion [%]	Yield of PhCHO [%][a])
1[b])	**1**	40	3	7	100	19
2[b])	**1**	40	3	7	100	54
3	**2**	20	–	4	100	65

[a]) Yields were determined by GC analysis with mesitylene as internal standard. [b]) With molecular sieves (4 Å).

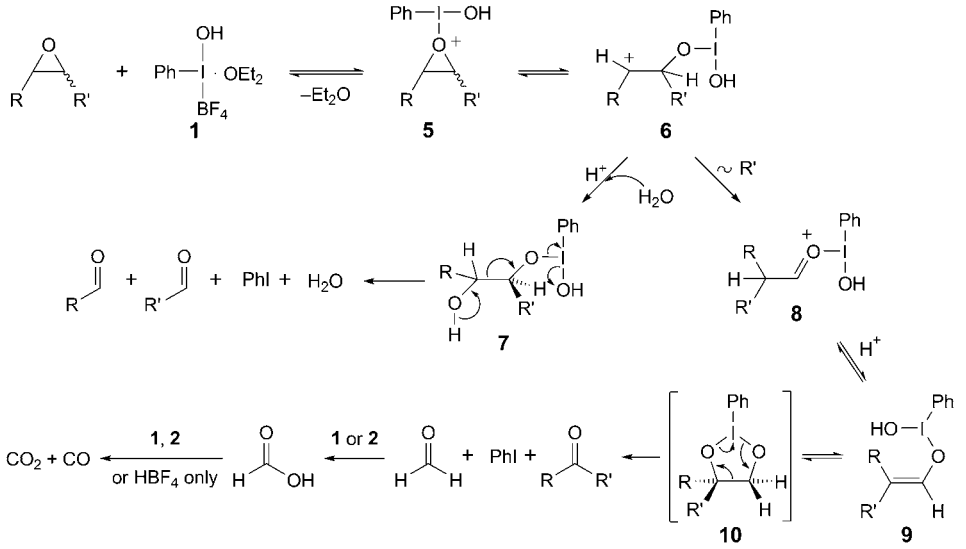
Scheme 1. *The Reaction of* rac-*(β,β-$^2H_2$)Styrene Oxide with PhIO and $HBF_4 \cdot OEt_2$* (50–55% in Et_2O)



and CO_2. The formation of CO and CO_2 was detected by $PdCl_2$/HCl reagent [16] and by saturated $Ba(OH)_2$ [17], respectively. Independent experiments with HCHO or HCOOH confirmed our assumption that these are converted rapidly to CO and CO_2 under these reaction conditions.

In summary, we have developed a protocol that allows selective C–C cleavage or rearrangement to carbonyl compounds of aryl epoxides.

Scheme 2. *Proposed Reaction Mechanism for Oxidative C–C Cleavage and Rearrangement Reactions*



Experimental Part

General. All used substrate epoxides were prepared according to published procedures [18]. PhIO was prepared from (diacetoxyiodo)benzene according to [19]. (Diacetoxyiodo)benzene, *rac-trans*-stilbene oxide, (α,α,α-$^2H_3$)acetophenone, and solvents were obtained commercially from *ABCR*, *Sigma-Aldrich*, *Fluka*, *Alfa Aesar*, and *Acros.* CH_2Cl_2 was dried over K_2CO_3, freshly distilled, and stored under Ar prior to use. TLC: Silica gel *60 F_{254} 25* aluminium sheets, 20 × 20 cm, from *Merck KGaA Co.*, D-Darmstadt. ^{1}H- and ^{13}C-NMR spectra: *Varian 300* and *Bruker 500* spectrometer; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. GC/MS: *Thermo TSQ 700*; GC (*Varian 3400*, achiral GC column *Macherey-Nagel optima 5MS*, 30 m × 0.25 mm, 0.25 μm film); in *m*/*z*.

General Procedure for the Rearrangement Reaction of Epoxides (*Table 1*, *Entries 1*, *3–5*, *7*, *8*, and *10*; *Table 2*, *Entries 1–6*; *Table 3*, *Entries 1* and *2*). In a 100-ml two-necked flask equipped with two bubble counters, which are connected and filled with the CO_2 detection reagent ($Ba(OH)_2$) and with the CO detection reagent ($PdCl_2$/HCl in H_2O), resp., epoxide (4.1 mmol, 1 equiv.) was dissolved in abs. CH_2Cl_2 (15 ml) under Ar. If necessary, 100 μl of mesitylene or 100 mg of 1,4-dichlorobenzene as internal standards were added (*Table 1*, *Entries 3* and *10*; *Table 2*, *Entries 1–6*; *Table 3*, *Entries 1* and *2*). Iodosylbenzene (1.9 g, 8.63 mmol, 2.1 equiv.) and *ca.* 5 g of molecular sieves (4 Å) were added (except for *Entry 3*, *Table 1*). Under stirring, 780 μl (2.89 mmol, 0.7 equiv., 50–55% in Et_2O) of $HBF_4 \cdot OEt_2$, diluted with abs. CH_2Cl_2 to the total volume given in *Tables 1–3*, was added dropwise to the suspension using a syringe pump. During the reaction, formation of $BaCO_3$ and Pd was observed in the bubble counters. After the reaction time given in *Tables 1–3*, the mixture was first washed with sat. $NaHCO_3$ soln. and extracted twice with Et_2O. The org. phase was then washed with sat. $Na_2S_2O_3$ soln., dried (Na_2SO_4), and filtered. The solvent was removed under reduced pressure. In the case of *Entries 4* and *5* (*Table 1*), the product was isolated by column chromatography (CC; cyclohexane/AcOEt). In the case of *Entry 8* (*Table 1*), the products were derivatized to hydrazones and isolated by CC (cyclohexane/AcOEt).

The spectroscopic data obtained for benzophenone, PhCHO, and acetophenone matched the published data [20].

General Procedure for C–C Oxidative Cleavage Reaction of Epoxides (*Table 1*, *Entries 2*, *6*, and *9*; *Table 2*, *Entry 7*; *Table 3*, *Entry 3*). In a two-necked flask equipped with two bubble counters, which are connected and filled with the CO_2 detection reagent ($Ba(OH)_2$) and with the CO detection reagent

($PdCl_2$/HCl in H_2O), the epoxide (4 mmol, 1 equiv.) was dissolved in 20 ml of abs. CH_2Cl_2. Iodosylbenzene (1.32 g, 6 mmol, 1.5 equiv.) was added. In the case of *Entry 6* (*Table 1*), 100 µl of mesitylene as internal standard was added to the suspension. Under stirring, 630 µl of HBF_4 (4.82 mmol, 1.2 equiv., 48% in H_2O) was added dropwise within 10 min (TLC control). No precipitation was observed in the bubble counters. After the reaction time indicated in *Tables 1–3*, the reaction mixture was worked up depending on the substrate as follows.

Isolation of Products by CC (*Table 2a*, *Entry 7*). The reaction mixture was first washed with sat. $NaHCO_3$ soln. and extracted twice with Et_2O. The org. phase was dried (Na_2SO_4) and filtered. The solvent was removed under reduced pressure. The products were isolated by CC (cyclohexane/AcOEt).

Isolation of Product as Hydrazone Derivative (*Table 1*, *Entries 2* and *9*; *Table 2b*, *Entry 3*). The reaction mixture was slowly concentrated to a total volume of *ca.* 4–5 ml. 2,4-Dinitrophenylhydrazine soln. was added, whereby a precipitate formed which was filtered and dried. In the case of *Entry 9* (*Table 1*), the products were isolated by CC (cyclohexane/AcOEt). Preparation of 2,4-dinitrophenylhydrazine soln.: 2.26 g of 2,4-dinitrophenylhydrazine (8 mmol, 2 equiv., 70%), 8.7 ml of conc. H_2SO_4, and 13 ml of H_2O were mixed. To the orange-colored soln., 42 ml of tech. EtOH was added. The soln. was then stirred for 10 min at r.t.

Benzaldehyde 2-(2,4-Dinitrophenyl)hydrazone. ^{1}H-NMR (300 MHz, (D_6)DMSO): 11.7 (br. *s*, CHNN*H*); 8.88 (*d*, *J* = 2.7, 1 arom. H); 8.73 (*s*, C*H*NNH); 8.43–8.36 (*dd*, *J* = 2.70, 9.70, 1 arom. H); 8.15–8.10 (*d*, *J* = 9.70, 1 arom. H); 7.85–7.75 (*dd*, *J* = 4.2, 2.06, 2 arom. H); 7.54–7.46 (*m*, 3 arom. H).

Benzophenone 2-(2,4-Dinitrophenyl)hydrazone. ^{1}H-NMR (300 MHz, (D_6)DMSO): 11.56 (*s*, CHNN*H*); 8.88 (*d*, *J* = 2.7, 1 H of $(NO_2)_2C_6H_3$); 8.66 (*d*, *J* = 7.3, C*H*NNH); 8.41–8.35 (*dd*, *J* = 2.70, 9.70, 1 H of $(NO_2)_2C_6H_3$); 7.86 (*d*, *J* = 9.70, 1 arom. H); 7.46–7.27 (*m*, 10 arom. H).

Synthesis of rac-*1-Phenyl(2,2,2-$^2H_3$)ethan(^2H)ol.* $LiAlH_4$ (3.39 g, 89.4 mmol, 1.1 equiv.) was suspended in 40 ml of abs. THF under Ar. The suspension was cooled in an ice bath, and 10 g of (*α*,*α*,*α*-$^2H_3$)acetophenone (81.3 mmol, 1 equiv.) in 40 ml of THF were added dropwise. The mixture was stirred for 2 h at r.t. (TLC control). Subsequently, cooled D_2O was added dropwise to the mixture cooled in an ice bath. The mixture was then diluted with DCl soln. (35% in D_2O) until dissolution of the precipitated salt, and extracted several times with Et_2O (abs.). The org. phase was dried (Na_2SO_4) and filtered. The solvent was removed under reduced pressure. Yield: 98%. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.28 (*m*, 5 arom. H); 4.92 (*s*, PhC*H*OCD_3).

Synthesis of (β,β-$^2H_2$)Styrene. In a 10-ml two-necked flask, equipped with a microdistillation apparatus and a dropping funnel, a pressure of 60 mbar was adjusted. $KHSO_4$ (370 mg, 2.72 mmol, 0.17 equiv.) was heated to 180°. A mixture of 2.00 g of *rac*-1-phenyl(2,2,2-$^2H_3$)ethan(^{2}H)ol (16 mmol, 1 equiv.) and of 5 mg of *p*-(*tert*-butyl)catechol (0.03 mmol) was then added dropwise to the heated $KHSO_4$ slowly, and the product formed was distilled fractionally. Yield: 59%. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.46–7.22 (*m*, 5 arom. H); 6.72 (*s*, PhC*H*CD_2).

Synthesis of rac-*(β,β-$^2H_2$)Styrene Oxide. rac-*(β,β-$^2H_2$)Styrene (376 mg, 3.5 mmol, 1 equiv.) was dissolved in 20 ml of CCl_4, and the soln. was cooled in an ice bath. *meta*-Chloroperbenzoic acid (*m*-CPBA; 1.3 g, 5.3 mmol, 1.5 equiv., 70–75%) was added portionwise over 3 h to the soln. The mixture was then slowly warmed to r.t. and stirred for 1 h (TLC control). *m*-CBA and unreacted *m*-CPBA were removed by washing the soln. with $NaHCO_3$ soln. and four times with 1M NaOH soln., resp. The org. phase was extracted with Et_2O, dried (Na_2SO_4), and filtered. The solvent was removed under reduced pressure. Yield: 94%. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.24 (*m*, 5 arom. H); 3.86 (*s*, PhC*H*(O)CD_2).

Oxidative Rearrangement and Cleavage of rac-*(β,β-$^2H_2$)Styrene Oxide. rac-*(β,β-$^2H_2$)Styrene oxide (234 mg, 2.2 mmol, 1 equiv.) was dissolved in 10 ml of abs. CH_2Cl_2 under Ar. PhIO (622 mg, 2.82 mmol, 1.3 equiv.) and *ca.* 5 g of molecular sieves (4 Å) were added to the soln. Under stirring, 738 µl (2.91 mmol, 1.3 equiv., 50–55% in Et_2O) of $HBF_4 \cdot OEt_2$, diluted with abs. CH_2Cl_2 to a total volume of 5 ml, was added dropwise to the suspension using a syringe pump with a drop rate of 2.5 ml/h. The mixture was stirred for another h and then washed with sat. $NaHCO_3$ soln. The org. phase was washed with sat. $Na_2S_2O_3$ soln. and extracted twice with CH_2Cl_2, dried ($MgSO_4$), and filtered. The products were isolated by CC (petroleum benzine (30/50)/Et_2O 30:1). The ratio PhCHO/PhCDO was determined by ^{1}H-NMR spectroscopy as 1:2.

(2H1)Benzaldehyde (= *(*formyl-*2H)Benzaldehyde*). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.89 (*d*, 2 arom. H); 7.67 – 7.46 (*td*, *J* = 7.19, 1.39, 1 arom. H); 7.57 – 7.49 (*t*, *J* = 7.30, 2 arom. H).

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