

Hypervalent Iodine: Introduction, Synthesis and its Applications

Dr. K. A. Sasane

Department of Chemistry, Abasaheb Marathe Arts & New Commerce, Science
College, Rajapur, Ratnagiri 416702, Maharashtra, India

E-mail: kulsasane007@gmail.com

Abstract:

Hyper iodine reagents are readily available, easy preparative procedures, and mild reactivity with good stability. The hypervalent iodine reagents have become reagents of interest to organic chemists. They can be used for many transformations like ring expansion reaction, ring closure reaction, single electron transfer reaction, oxidation etc. In this chapter study literature on hypervalent iodine compounds, their synthesis and applications are listed.

Keywords: Hypervalent iodine, DIB, IBX, Cyclisation, Synthesis

Introduction:

1.1 Hypervalent Iodine Reagents:

French chemist Bernard Courtois was discovered Iodine in 1811 and it was named by J. L. Gay Lussac in 1813. Its name derives from the Greek word *iodes*, sense "violet-colored," reflecting both the characteristic lustrous, deep purple colour of resublimed crystalline iodine as well as the colour of its vapours. It can be found in seaweed and brine wells.

Iodine

Element number 53

Atomic weight 126.9

Oxidation state

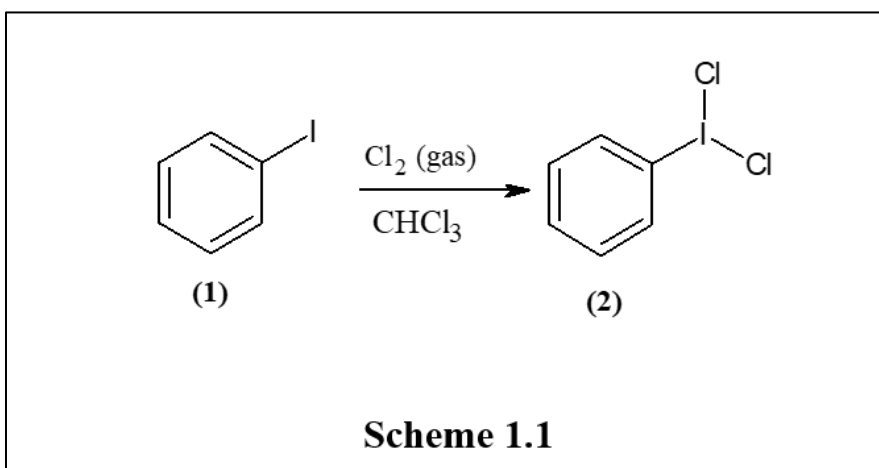
Main I-1

Others I0, I+3, I+5, I+7

Electronic Configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^5$

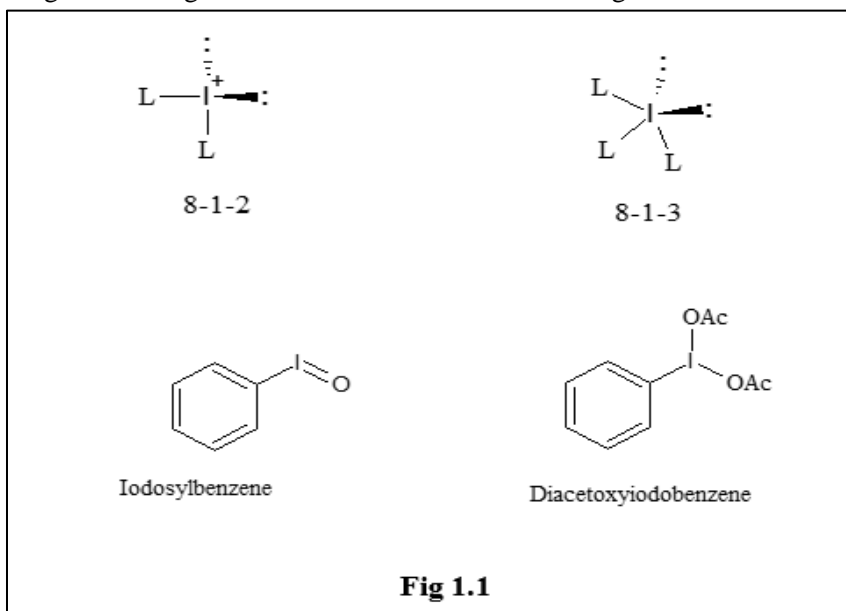
Hypervalency

In numerous compounds, the elements belonging to the 15–18 groups exhibit greater oxidation states than normal valency (Musher, 1969). "Hypervalency" refers to an atom's ability to expand its valence shell outside of the bounds of the Lewis octet rule within a molecular entity. The relocation of electrons from the core, hypervalent atom to the nonbonding molecular orbitals it creates with (more electronegative) ligands is implied by an explanation of hypervalency.



1.1.2 Nomenclature of hypervalent iodine compounds:

The nomenclature of hypervalent iodine compounds is based on the oxidation states of the core iodine atom. Numerous compounds with valences ranging from 1 to 5 are known to exist. These compounds are typically coordinated with 2-4 different ligands (Varvoglis, 1992). Figures 1.1 illustrate four major structural kinds of hypervalent iodine reagents together with general notations for each iodine reagent.



1.1.3 Iodine (V) compounds: Also named $\lambda 5$ -iodanes. Represented C in Fig. 1.2

1.1.4 Iodine (III) compounds: Also named $\lambda 3$ -iodanes according to IUPAC

Recommendations

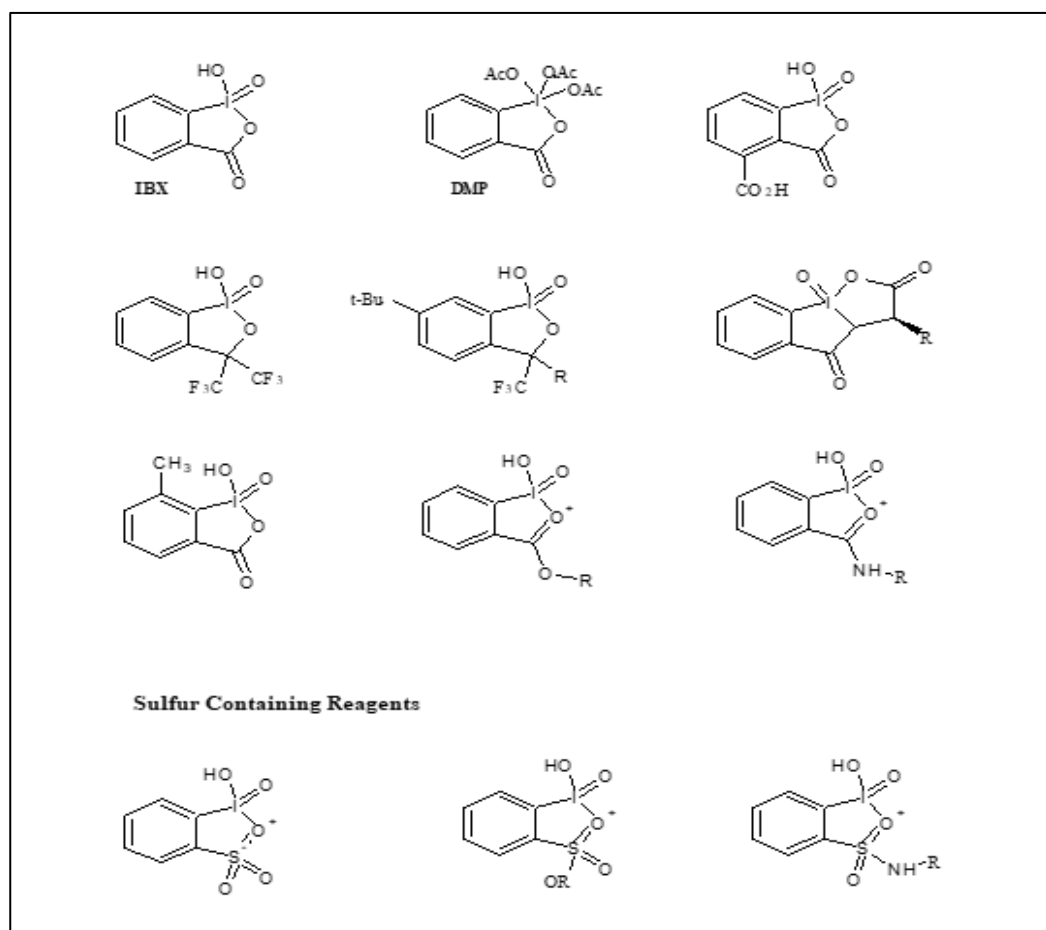


where R = Carbon ligand

X = O or N Ligand

Fig 1.2

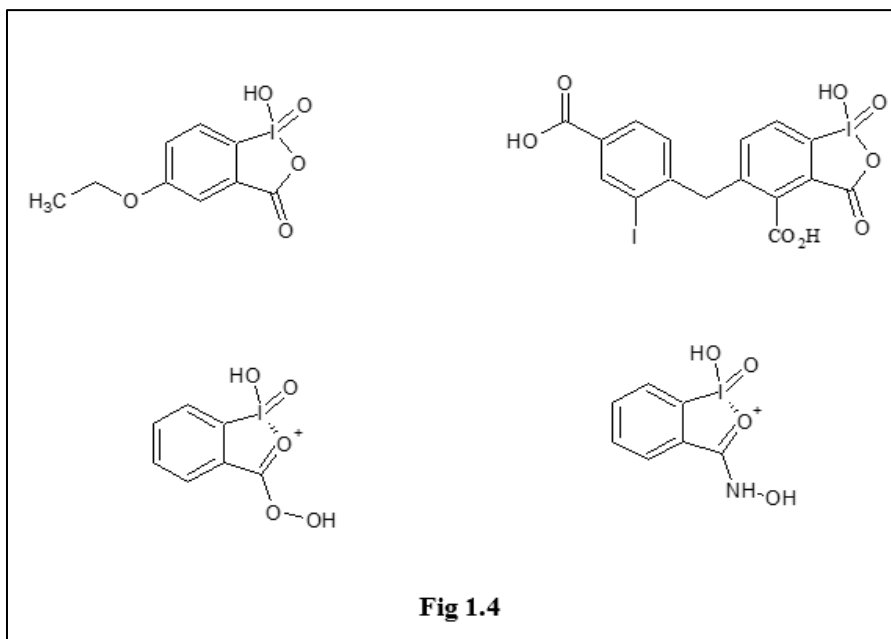
Some of the Examples of hypervalent iodine (IV) reagents, derivatives of IBX and other cyclic pentavalent reagents are shown below (Fig 1.3)



These reagents are employed in a variety of transformations as oxidizing agents for amino alcohols protected by carbamate, as well as primary, secondary, benzylic, allylic, and terpene alcohols, resulting in the corresponding aldehydes or ketones in

remarkable yields and purities.

d) Polymer supported Hypervalent (IV) reagents:



1.2 Applications of IBX:

- ❖ Oxidative cleavage of vicinal 1, 2-diols.
- ❖ The oxidative transformation of threonines involved the α -hydroxylation and oxidation of a secondary alcohol to a ketone (Harding, 2009).
- ❖ Dehydrogenation of tetrahydro-carbolines to their aromatic forms.
- ❖ Primary Carboxamides Oxidatively Transform into One-Carbon Dehomologated Nitriles
- ❖ Synthesis of α - β Unsaturated Systems from Alcohols and Ketones
- ❖ Oxidation of primary alcohol to carboxylic acid
- ❖ Oxidation of secondary alcohol to ketone.
- ❖ α -Hydroxylation of Alkynyl Carbonyl Systems
- ❖ Oxidation of various phenols to *o*-quinones.
- ❖ Key step of the total synthesis of the streptomycin maritimus metabolite, wailupemycin B.
- ❖ Oxidation of primary alcohols or aldehydes to N-hydroxysuccinimide esters.
- ❖ Oxidation of alcohols, ketones, and aldehydes to the corresponding α - β unsaturated species.
- ❖ Oxidation of alkyl-substituted aromatic compounds at the benzylic position to the corresponding carbonyl derivatives.
- ❖ Oxidation of alcohols, secondary amines can be oxidized with IBX in DMSO to yield the corresponding imines.

1.2.1 Applications of DMP:

The utilization of DMP in the complete synthesis of CP-molecules, lead structures for cardiovascular and anticancer medications disclosed by Nikolaou and colleagues, is the greatest example of the compound's special oxidizing capabilities.

- ❖ The allylic aldehydes and alkyl acetylates' Baylis-Hillman adducts can be effectively oxidized to get the appropriate α -methylene- β -keto esters.
- ❖ Synthesis of Cyclic enecarbamates from oxidation of α -hydroxy carbamates.
- ❖ Synthesis of cyclic acetoxy acetals from 1, 4 diols.
- ❖ Polyfluorinated alcohols can be oxidised to respective aldehydes.
- ❖ Primary alcohol can be oxidised to α , β unsaturated esters in presence of witting ylide.
- ❖ Deoxygenation of aldoximes as well as ketoximes to respective ketones.
- ❖ Conversion of matching aldehydes and thioles into thioesters under mild circumstances.
- ❖ α - bromination of α - β unsaturated ketones.
- ❖ α - tosylation of secondary alcohol.
- ❖ α - bromination of 1, 3 diketones.

1.3 Preparation of trivalent reagents:

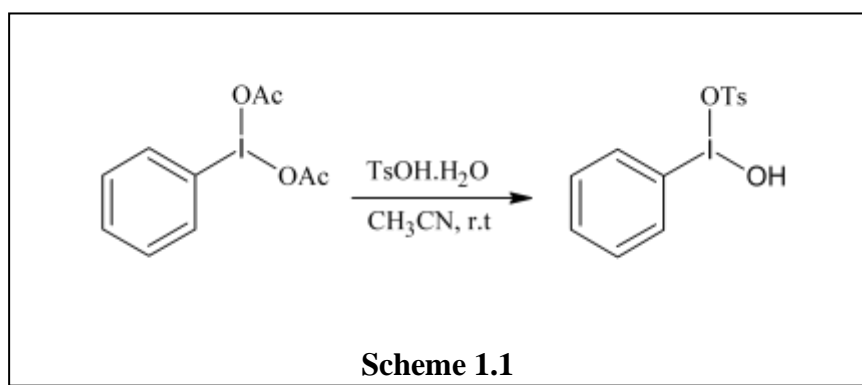
a) (Difluoroiodo) arenes

This is an extremely potent fluorinating reagent that can be made by fluorinating iodoarenes with strong reagents like XeF₂, F₂, ClF, and BrF₅. Mercuric oxide and aqueous HF were previously used in a process where they reacted with (Dichloroiodo) arenes in MDC. This method's drawback is the significant amount of hazardous HgO required to remove the chloride ion from the reaction mixture. Iodosylarenes are treated with 40–46% aqueous hydrofluoric acid, and the resultant (Dichloroiodo) arenes are then crystallized from hexane in a convenient modified process that does not require the use of HgO (Hara et al., 2002; Wirt et al., 2005; DiMagno et al., 2008). It is crucial that the Iodosylarenes be utilized in this technique freshly manufactured.

b) Koser's reagent

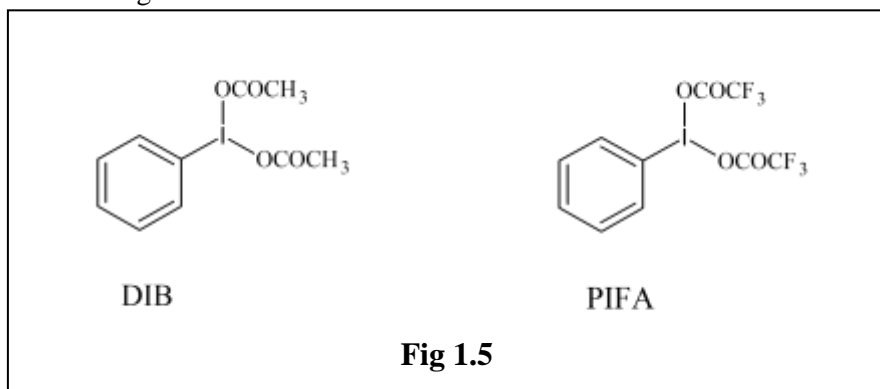
Typically, a ligand exchange reaction between (diacetoxyiodo) arenes and p-toluenesulfonic acid monohydrate in acetonitrile is used to prepare [hydroxy (tosyloxy) iodo] arenes (Scheme 1.1). Katzenellenbogen et al., 2007; Togo et al., 2002; 2005; 2001; Kita et al., 2004; 2005; Zhdankin et al., 2008; Zhang et al., 2005; Wirth et al., 2001; 2005).

Iodoarenes and mCPBA react in one pot at room temperature with sulfonic acids and a tiny amount of chloroform, providing a straightforward modified method for preparing several [hydroxy (sulfonyloxy) iodo] arenes. Recently, novel reusable organic trivalent iodine reagents based on biphenyl and terphenyl were prepared using this modified process.

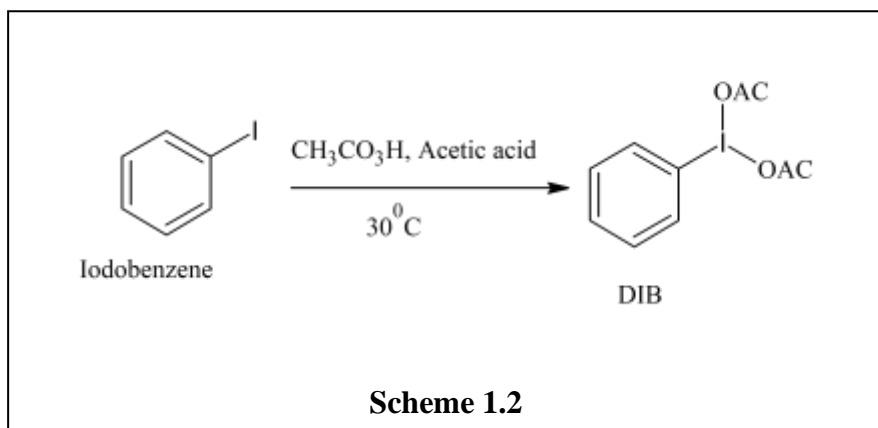


1.3.1 (Diacetoxyiodo) benzene preparations:

(DIB) is a synthetic precursor to several related compounds and one of the first reagents in this family to be studied. Of these derivatives, [Bis (trifluoroacetoxy) iodo] benzene (BTI) is important since it has various intriguing uses in contemporary chemical synthesis. It has been noted that the synthetic characteristics of trivalent iodine compounds are often comparable to those of derivatives of lead and thallium, albeit with better yields and improved toxicity, making them more suitable for use in pharmaceutical production settings.



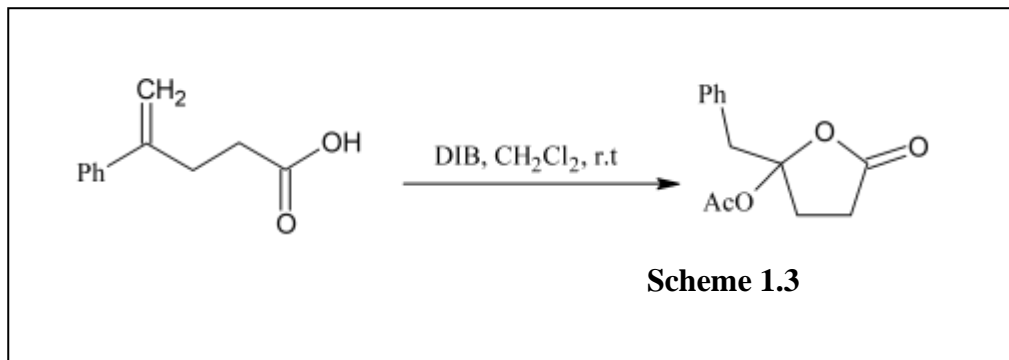
a) From Iodoarenes:



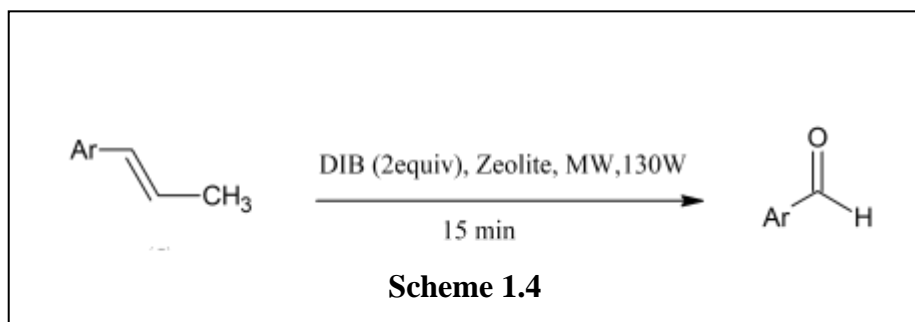
The easiest and most often used method for preparing a variety of (diacetoxyiodo)-substituted arenes and hetarenes on a small scale is the oxidation of iodoarenes with sodium perborate in acetic acid at 40 °C.

1.4 Applications of hypervalent iodine (III) reagent:

I. Lactonization:

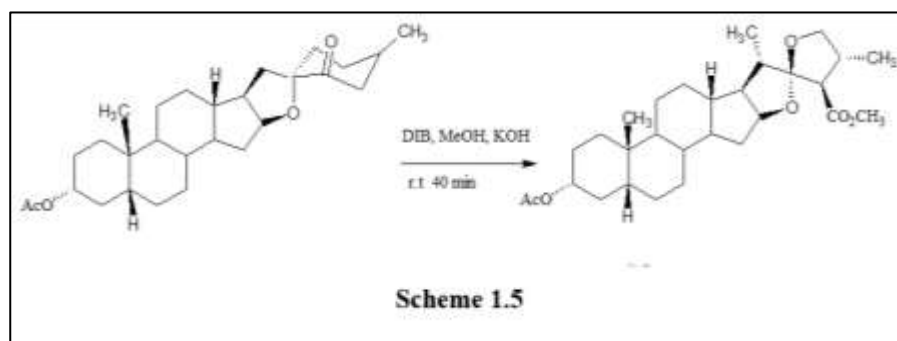


A multicomponent reaction of allenes, diaryl diselenides, DIB and alcohols or acids formed substituted allyl derivatives in moderate yields (Huang et al., 2007).



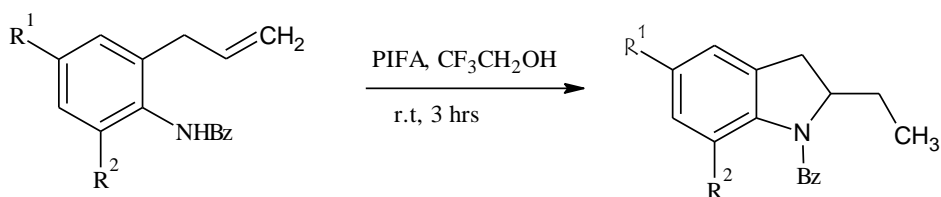
V. Oxidative transformations of steroidal substrates:

An axial acetoxy group was introduced at position C-23 of the side chain in the instance of steroidal substrate with DIB and boron trifluoride etherate in acetic acid (Iglesias-Arteaga et al., 2006; 2007).

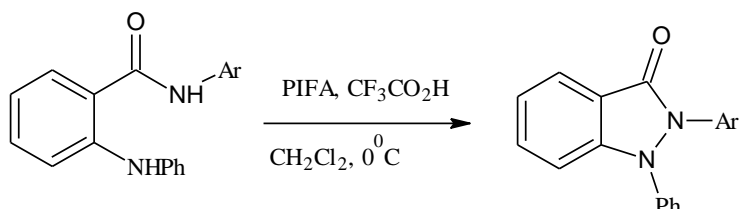


VII. Oxidative Cationic Cyclization, Rearrangements, and Fragmentations:

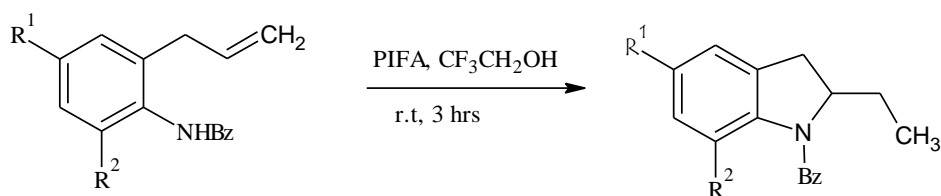
The synthesis of indoline derivatives from anilides and indazol-3-ones from anthranilamides (Scheme 1.6; Dominguez et al., 2005, 2006, 2007) are two recent exemplary instances. Pyrrolidinones have been synthesized from alkynylamides with the assistance of PIFA.



Scheme 1.6



Scheme 1.7



Scheme 1.8

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