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N-Halosuccinimide/$AgNO_3$-Efficient Reagent Systems for One-Step Synthesis of 2-Haloglycals from Glycals: Application in the Synthesis of 2C-Branched Sugars via Heck Coupling Reactions

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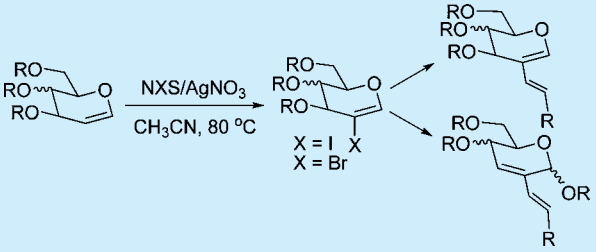
Supporting Information

ABSTRACT: An expedient one-step synthesis of 2-iodoglycals and 2-bromoglycals from glycals using NIS/$AgNO_3$ and NBS/$AgNO_3$ as reagent systems has been developed. The utility of these 2-haloglycals has been demonstrated by converting them into 2C-branched glycals via the Heck coupling reaction. Ferrier reaction of tri-*O*-acetyl-2-iodoglycals followed by Heck coupling reaction with methyl acrylate leads to 2C-branched *O*-glycosides.



Carbohydrates play a crucial role in many biological processes such as cell development, cell−cell and cell−viral recognition, cell adhesion, inflammation, the immune response, etc., and have become a central theme in glycochemistry and glycobiology.[1] Apart from the synthesis of biological glycoconjugates, a wide range of synthetic carbohydrates are also being developed that may act as carbohydrate mimetics. Among them, C-branched sugars are of much interest as they are part of naturally occurring important antibiotics, macrolides, and some polysaccharides.[2] More recently, 2C-branched sugars have also been identified as sugar mimetics of N-acetyl sugars that are involved in the biosynthesis of lipids[3] and as a result they have become important targets of synthetic carbohydrate chemists. Thus, for example, Linker et al.[4] made a platform for the synthesis of 2C-branched sugars using a novel ceric ammonium−nitrate mediated radical reaction on glycals.

Following this, more reports have appeared in the literature involving the ring-opening reaction of 1,2-cyclopropanated sugars,[5] 2-formyl glycals,[6a,b] and 2-nitrosugars.[6c,f] Besides these, 2-haloglycals have become a new entry to the 2C-functionalized glycals and are widely used as important synthons in carbohydrate chemistry.[7] Thus, 2-iodo- and 2-bromoglycals have been used in the synthesis of 2C-aryl glycosides,[7e] the oxadecalin core of phomactin A,[8] and biologically active scaffolds such as chromans and isochromans.[9] In these syntheses, palladium-catalyzed domino, Sonogashira, and Suzuki−Miyaura coupling reactions have been employed.

Apart from this, 2-chloroglycals are used in the synthesis of benzannulated sugars via organolithium intermediates using *t*-BuLi as a base.[10] However, 2-bromo- and 2-iodoglycals are more reactive and hence more often utilized. In spite of their importance, there is no convenient method reported for their synthesis. One of the known methods involves two steps in which glycals are first treated with a source of iodonium ion in aqueous medium to provide the corresponding 2-deoxy-2-iodopyranoses, which are then eliminated with Ph_2SO/Tf_2O to give the corresponding 2-iodoglycals.[7b] The other method involves treatment of glycals with Br_2 or SO_2Cl_2 to give the corresponding dibromo or dichloro derivatives, which are subjected to HBr or HCl elimination using DBU as a base to give 2-bromo-[9b] and 2-chloroglycals,[7c] respectively.

We have been involved in the functionalization of glycals to obtain important synthetic intermediates such as 2-nitroglycals, 2-deoxy-*O*-glycosides, 2-deoxy-1-glycopeptides, 1,2-diaminosugars, 2-chloro-1-acetamido sugars, and 2-iodo-1-azido sugars.[11,6f] In continuation of our efforts in this direction, we wish to report an extremely simple one-step synthesis of 2-haloglycals from glycals using *N*-halosuccinimides and a catalytic amount of silver nitrate.

We recently reported the synthesis of 2-nitroglycals from glycals using two different reagent systems.[12] The first method involves[12a] the use of an acetyl chloride−silver nitrate−acetonitrile reagent system which affords the 2-nitroglycals or 2-nitro-1-acetamido glycosides depending on the experimental conditions. The second one employs[12b] a combination of tetrabutylammonium nitrate−trifluoroacetic anhydride−triethylamine as a reagent system which gives 2-nitroglycals as the sole products. In the course of developing new reagents for the synthesis of 2-nitroglycals, we came across a literature report about the use of a combination of *N*-bromosuccinimide−$AgNO_3$ that acts as a nitrating agent for various substituted aromatics.[13] However, the nature of reactivity of such a reagent combination is not clear, particularly how it acts as a source of nitronium ion. If it is indeed a source of a nitronium ion then we expect it to convert glycals to 2-nitroglycals. On the other hand, it is well-known that *N*-halosuccinimides (NXS; X = Cl, Br, I) are used as excellent sources for the halogenations of olefins and aromatics. For

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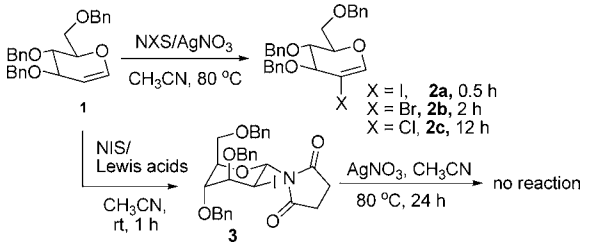
example, Olah et al. reported[14] the halogenation of deactivated aromatic systems with *N*-halosuccinimides along with BF_3–H_2O as a Lewis acid catalyst. Keeping these observations in mind, we were interested in finding out how the reagent combination (NXS/$AgNO_3$) behaves with glycals and expected them to give 2-nitroglycals in line with the nitration of aromatics (vide supra).

First, we performed the reaction of tri-*O*-benzyl-D-glucal **1** with *N*-iodosuccinimide (NIS)/$AgNO_3$ in acetonitrile. To our surprise, we isolated tri-*O*-benzyl-2-iodoglucal **2a** (Scheme 1)

Scheme 1. Reaction of Tri-*O*-benzyl-D-glucal with NXS/$AgNO_3$ (or Lewis Acids)

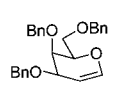
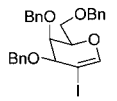
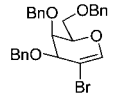
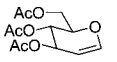
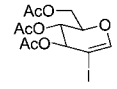
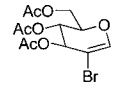
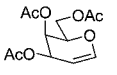
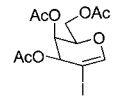
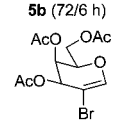
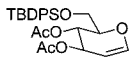
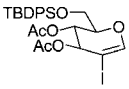
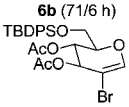
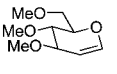
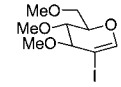
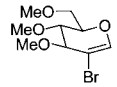
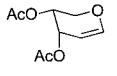
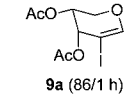
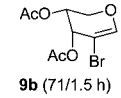
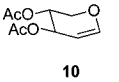
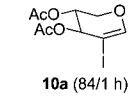
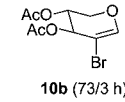
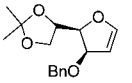
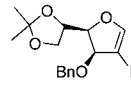
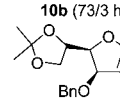


as the sole product. Initially, we had used 1 equiv of $AgNO_3$ and 1.2 equiv of NIS with respect to the glucal **1** and heated the reaction mixture at 80 °C for 0.5 h, which gave **2a** in 70% yield. Since the product did not contain any elements of a nitro group, we carried out the reaction of **1** with NIS in the presence of a catalytic amount of $AgNO_3$ (20 mol %, an optimized amount), which gave **2a** in 72% yield. We also studied the reaction with various Lewis acids such as $BF_3{\cdot}OEt_2$, AgOTf, $InCl_3$, $Yb(OTf)_3$, and $In(OTf)_3$. However, we did not observe the formation of the expected 2-iodoglucal product **2a**. Instead, the isolated product was 2-iodo-1-succinimidyl glucoside **3** (Scheme 1), which is reported[15] to be formed without the addition of a Lewis acid also. In order to confirm if the formation of **2** proceeds via **3**, we treated it with $AgNO_3$ at 80 °C in acetonitrile, but the starting material was found unchanged even after 24 h. This implies that the reaction does not proceed via the addition product **3**.

Next, we screened the reactivity of other nitrates such as KNO_3, $NaNO_3$, and *n*-Bu_4NO_3, in place of $AgNO_3$, wherein the reactions took longer time and yields of **2** were very poor. Hence, we explored the reactivity of various protected glycals with *N*-halosuccinimides in the presence of a catalytic amount of $AgNO_3$. Thus, tri-*O*-benzyl-D-galactal **4** on treatment with NIS/$AgNO_3$ smoothly gave the corresponding 2-iodogalactal **4a** in 68% in 30 min. Acetyl-protected glycals **5** and **6** also underwent reactions to give the corresponding 2-iodoglycals **5a** and **6a** in very good yields (Table 1, column 3). These reactions were repeated on a 1 g scale, and comparable yields were obtained. Silyl-protected glucal **7** and methyl-protected glucal **8** were also treated with this reagent system to form the corresponding products **7a** and **8a**, respectively. Further, pentose sugars 3,4-di-*O*-acetyl-D-arabinal **9** and 3,4-di-*O*-acetyl-D-xylal **10** and furanose glycal **11** also gave the 2-iodo glycals **9a**, **10a**, and **11a**, respectively. Likewise, all of the protected glycals were treated with the *N*-bromosuccinimide/$AgNO_3$ reagent system, and the corresponding 2-bromoglycals **2b**–**11b** were formed in moderate to good yields (Table 1, column 4).

We then explored the reactivity of *N*-chlorosuccinimide (NCS)/$AgNO_3$ reagent system with tri-*O*-benzyl-D-glucal **1**.

Table 1. Syntheses of 2-Iodoglycals and 2-Bromoglycals from Various Protected Glycals[a]

entry	glycals	2-iodoglycals (% yield[b]/time)	2-bromoglycals (% yield[b]/time)
1	**1**	**2a** (72/0.5 h)	**2b** (63/2 h)
2	 **4**	 **4a** (68/0.5 h)	 **4b** (65/1 h)
3	 **5**	 **5a** (88/4 h)	 **5b** (72/6 h)
4	 **6**	 **6a** (82/3 h)	 **6b** (71/6 h)
5	 **7**	 **7a** (76/2 h)	 **7b** (68/5 h)
6	 **8**	 **8a** (63/15 min)	 **8b** (58/0.5 h)
7	 **9**	 **9a** (86/1 h)	 **9b** (71/1.5 h)
8	 **10**	 **10a** (84/1 h)	 **10b** (73/3 h)
9	 **11**	 **11a** (57/10 min)	 **11b** (35/30 min)

[a]Reaction conditions: glycals (0.24 mmol), NXS (0.28 mmol), $AgNO_3$ (0.048 mmol), CH_3CN (2.0 mL), N_2 atmosphere, 80 °C, [b]Isolated yields after purification by silica gel column chromatography.

However, the corresponding 2-chloroglucal product **2c** was isolated only in 20% yield, and the remaining starting material was recovered (Scheme 1). This might be because NCS is less reactive than NIS and NBS.

A plausible mechanism for the formation of 2-haloglycals is depicted in Scheme 2. *N*-Halosuccinimide acts as an electrophilic source in the presence of $AgNO_3$ and reacts with the double bond of a glycal to give the oxonium ion intermediate **C** along with the formation of silver succinimide **D**. The expunged nitrate ion then reacts with **C** to give another intermediate **E** which, under heating conditions, picks up a proton from C-2 in an intramolecular fashion to yield 2-haloglycals **F** and nitric acid. The silver succinimide **D** then reacts with the released HNO_3 to form succinimide and regenerates $AgNO_3$ for the catalytic cycle to resume. The ^1H NMR spectrum of the crude reaction mixture in the reaction of **6** with NIS/$AgNO_3$ clearly showed the presence of succinimide peaks at δ 2.6 and 8.7 in $CDCl_3$, confirming its formation as one of the products of the reaction. Interestingly, we isolated small amounts of AgI (and AgBr) in these reactions, which may act as a driving force for the reaction since other Lewis acids do not lead to the desired products.[16]

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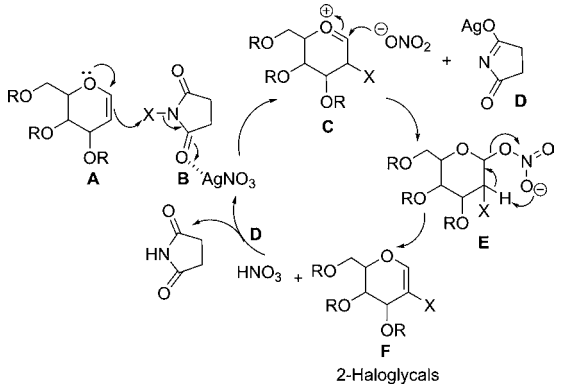
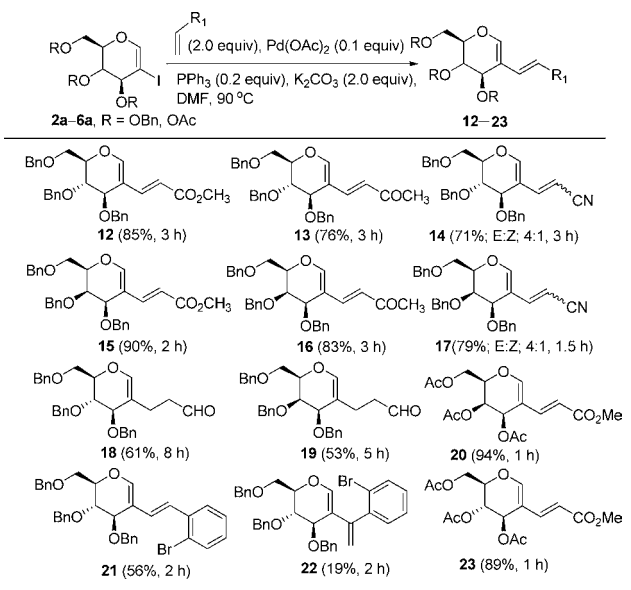
Scheme 2. Proposed Mechanism for the Formation of 2-Haloglycals



The palladium-catalyzed coupling reactions of vinyl halides with activated and nonactivated alkenes as well as aromatics are well recognized methods for C−C bond formation. 2-Bromoglycals have been extensively used in Pd-catalyzed reactions to annulate a further ring system.[9b,e] 2-Bromoglycals have also been utilized in Heck coupling reactions with simple olefins as well as activated olefins.[17] Having developed an efficient method for the preparation of 2-iodoglycals and 2-bromoglycals, we wished to explore the utility of 2-iodoglycals in the synthesis of 2-C substituted sugars which are present in numerous natural products.[18] We first attempted the Heck coupling reaction of tri-*O*-benzyl-2-iodoglucal **2a** with methyl acrylate using $Pd(OAc)_2/PPh_3$ and Et_3N in acetonitrile, which afforded the coupled product **12**. However, the reaction was slow and took 2 days for completion. A solvent change to DMF helped the reaction to proceed faster, and it took only 3 h to form **12** in 85% yield. Various combinations were used, and the most suitable catalyst combination was found to be $Pd(OAc)_2/PPh_3$, K_2CO_3 with DMF as a solvent.

Tri-*O*-benzyl-2-iodoglucal **2a** was also converted to the corresponding Heck-coupled products **13** and **14** using appropriate alkene acceptors (Scheme 3).

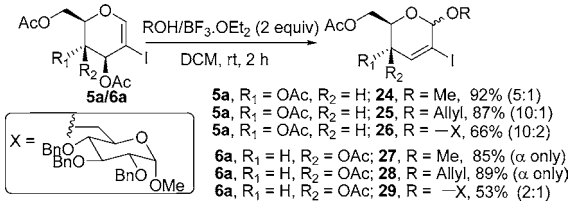
Scheme 3. Heck Reaction of 2-Iodoglycals with Different Alkenes



In a similar way, tri-*O*-benzyl-2-iodogalactal **4a** underwent Heck coupling with different acceptors to give the coupled products **15**−**17** in good yield. The reactions of tri-*O*-acetyl-2-iodoglycals **5a** and **6a** were also carried out with methyl acrylate, using Et_3N as a base, which gave the corresponding vinylic esters **20** and **23**. Then, we chose allylic alcohol as an acceptor for the Heck coupling reaction to access 2C-substituted glycals, and as per our expectation, the products **18** and **19** were formed in reasonable yield, as summarized in Scheme 3. Interestingly, the reaction of *o*-bromostyrene with **2a** gave two types of coupled products viz. dienes **21** and **22** in 3:1 ratio.

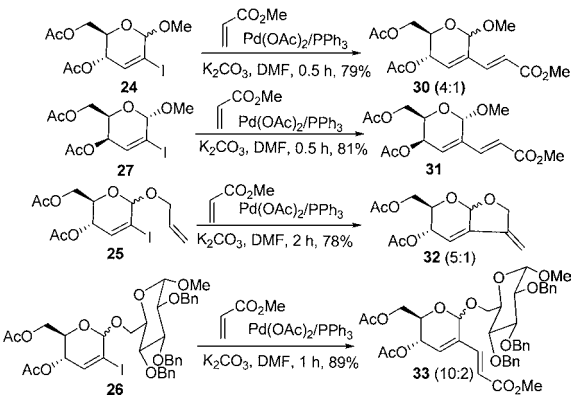
We next explored the utility of tri-*O*-acetyl-2-iodoglycals to obtain the corresponding 2,3-unsaturated *O*-glycosides using the Ferrier reaction. Thus, in reaction of **5a** with methanol and allyl alcohol in the presence of $BF_3{\cdot}OEt_2$, the reaction proceeded smoothly to furnish the corresponding Ferrier products **24** (anomeric ratio 5:1) and **25** in excellent yield. Compound **5a** underwent the Ferrier reaction with a monosaccharide donor HOX to form the corresponding disaccharide **26** (Scheme 4). Likewise, the tri-*O*-acetyl-2-iodogalactal **6a** underwent the Ferrier reaction to furnish the *O*-glycosylated products **27**−**29** in moderate to good yields (Scheme 4).

Scheme 4. Ferrier Reaction of Tri-*O*-acetyl-2-iodoglycals 5a and 6a



The 2,3-unsaturated sugars obtained from the Ferrier reactions were converted to the corresponding 2C-substituted *O*-glycosides using Heck coupling reactions. Thus, compound **24** upon treatment with methyl acrylate using $Pd(OAc)_2/PPh_3$ in DMF solvent, which smoothly gave the vinylic ester **30** in very good yield (Scheme 5). Likewise, the Ferrier product **27** was converted to the corresponding vinyl ester **31**. The *O*-allyl glucoside **25** was subjected to intramolecular Heck coupling reaction using $Pd(OAc)_2/PPh_3$ to give the bicyclic compound

Scheme 5. Heck Reaction of Ferrier Products with Methyl Acrylate



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32 in good yield. Also, disaccharide 26 underwent the Heck coupling reaction with methyl acrylate to give 2C-branched oligosachharide 33 in excellent yield. The resulting 2-C substituted glycosides can be employed as versatile intermediates in organic synthesis as well as sugar mimics.

In summary, we have developed a convenient one-step synthesis of 2-iodo- and 2-bromoglycals from various glycals using NIS/$AgNO_3$ and NBS/$AgNO_3$ as reagent systems. The applicability of these 2-haloglycals has been demonstrated by converting some of the iodoglycals to the corresponding Heck coupling products using various alkenes. Further, we have carried out a Ferrier reaction of tri-*O*-acetyl-2-iodoglycals followed by a Heck coupling reaction leading to 2C-branched *O*-glycosides.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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