A study of the mechanism of the azidophenylselenylation of glycals*

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Chemical and physicochemical studies of homogeneous azidophenylselenylation of glycals with diacetoxyiodobenzene, trimethylsilyl azide, and diphenyl diselenide in dichloromethane revealed that the most probable key reaction step is the formation of phenylselenyl azide, an azide radical donor. A method for azidophenylsulfenylation of glycals was proposed.

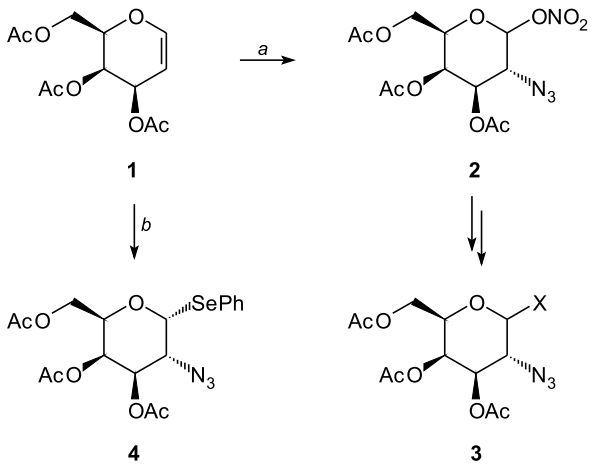
Key words: glycal, azidophenylselenylation, azide radical, phenylselenyl azide.

2-Amino-2-deoxy-α- and 2-amino-2-deoxy-β-D-glycopyranosyl residues are abundant structural elements of natural microbial and plant polysaccharides, glycoproteins, glycolipids, and other carbohydrate-containing compounds.[1—5] That is why modern carbohydrate chemistry needs new synthetic approaches for stereoselective introduction of the 2-amino-2-deoxy-α- and 2-amino-2-deoxy-β-D-glycopyranosyl residues upon assembling oligosaccharide chains. Glycosyl donors based on 2-azido-2-deoxy-D-glycopyranoses as synthetic precursors of the corresponding 2-amino-2-deoxy-α- and 2-amino-2-deoxy-β-D-glycopyranosides are most frequent in the synthesis of the aforementioned types of compounds.[1,5] Indeed, glycosylation with 2-azido-2-deoxy-D-glycopyranose derivatives allows the stereocontrolled formation of both α- and β-glycoside linkages. In addition, the use of glycosyl donors based on 2-azido- rather than 2-*N*-acylamino-2-deoxy-D-glycopyranoses can provide substantially more tactic scope for the design of synthetic schemes.

A search for novel types of efficient glycosyl donors based on 2-azido-2-deoxy-D-glycopyranoses is an interesting area in oligosaccharide synthesis.[1—6] Such compounds can be obtained in various ways.[7] The most widely used methods involve azidonitration of glycals, *e.g.*, galactal **1** (Scheme 1, pathway *a*) followed by the conversion of the resulting azido nitrate **2** into glycosyl donor **3** through replacement of the anomeric nitro group[8] by a halogen atom or an alkyl, arylthio, or trichloroacetimidate group. Though being currently very popular, this method is laborious because of many steps involved and hence more efficient synthetic procedures should be developed.

The much more promising type of glycosyl donors based on 2-azido-2-deoxysugars are 2-azido-2-deoxyphenylselenoglycosides, which can be obtained in one step directly from glycals under azidophenylselenylation conditions[9—11] (APS reaction) (see Scheme 1, reaction *b*).

Scheme 1



X = Hal, SR, $OC(NH)CCl_3$

The present work was intended to continue our investigations of the APS reaction.[10,11] Here we studied its mechanism and selected the conditions for a similar process leading to 2-azido-2-deoxythioglycoside derivatives through the use of organosulfur compounds.

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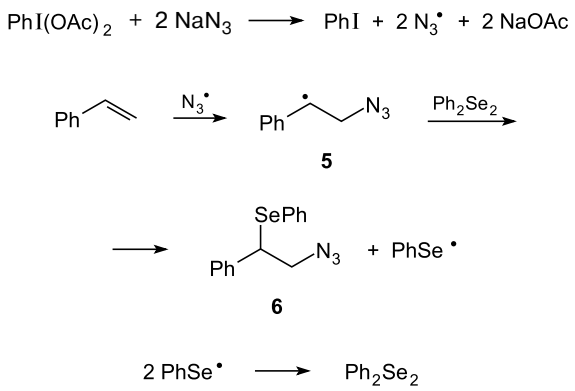
Results and Discussion

The first documented examples of the APS reaction of an alkene with diacetoxyiodobenzene, sodium azide, and diphenyl diselenide in dichloromethane were transformations of simple olefins, *e.g.*, styrene[9a] (Scheme 2). An analysis of the reaction products suggested a radical addition mechanism involving initial oxidation of the azide anion with diacetoxyiodobenzene into an azide radical followed by the formation of carbon radical **5** *via* anti-Markownikoff addition to the olefin; scavenging of the radical with diphenyl diselenide gives adduct **6**.

Scheme 2

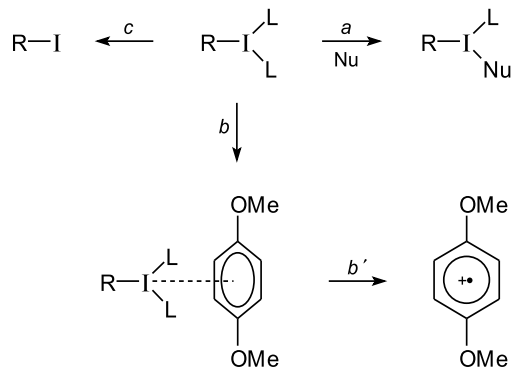


Unfortunately, when applied to preparative azidophenylselenylation of glycals, this procedure[9a] and its versions[9b–e] have limitations that preclude scale up of the starting reagents.[10] For homogenization of the reaction mixture, we have modified[10] the APS reaction by using trimethylsilyl azide as an azide anion source instead of sodium azide insoluble in CH_2Cl_2. This procedure is more suitable for preparative purposes, gives reproducible results, allows scaling of the starting reagents, and can be used for various O-protected mono- and oligosaccharide glycal substrates including complex heterosaccharide derivatives with the *N*-acetylneuraminic acid residue.[10,11] We also studied the influence of the glucal structure on the stereoselectivity of the APS reaction and the efficiency of formation of the corresponding *gluco*- and *manno*-adducts.[11]

Another problem to be solved during the study of the APS reaction was the replacement of expensive and toxic diphenyl diselenide by a sulfur derivative in the glycal transformations under discussion because the resulting thioglycosides seem to be more promising reagents for preparative oligosaccharide synthesis than selenoglycosides.

For deeper insight into the APS reaction mechanism, we considered the known types of transformations of iodine(III) derivatives (Scheme 3): ligand exchange at the iodine atom[12] (pathway *a*), formation of a radical cation (pathway *b*; examined earlier[13] in detail for reactions of iodobis(trifluoroacetoxy)benzene with a number of arenes as examples), and oxidative ligand elimination (pathway *c*). Apart from the azide anion, possible nucleophiles in the APS reaction are also glycal and diphenyl diselenide (intermediates **7** and **9**, respectively; Scheme 4).

Scheme 3

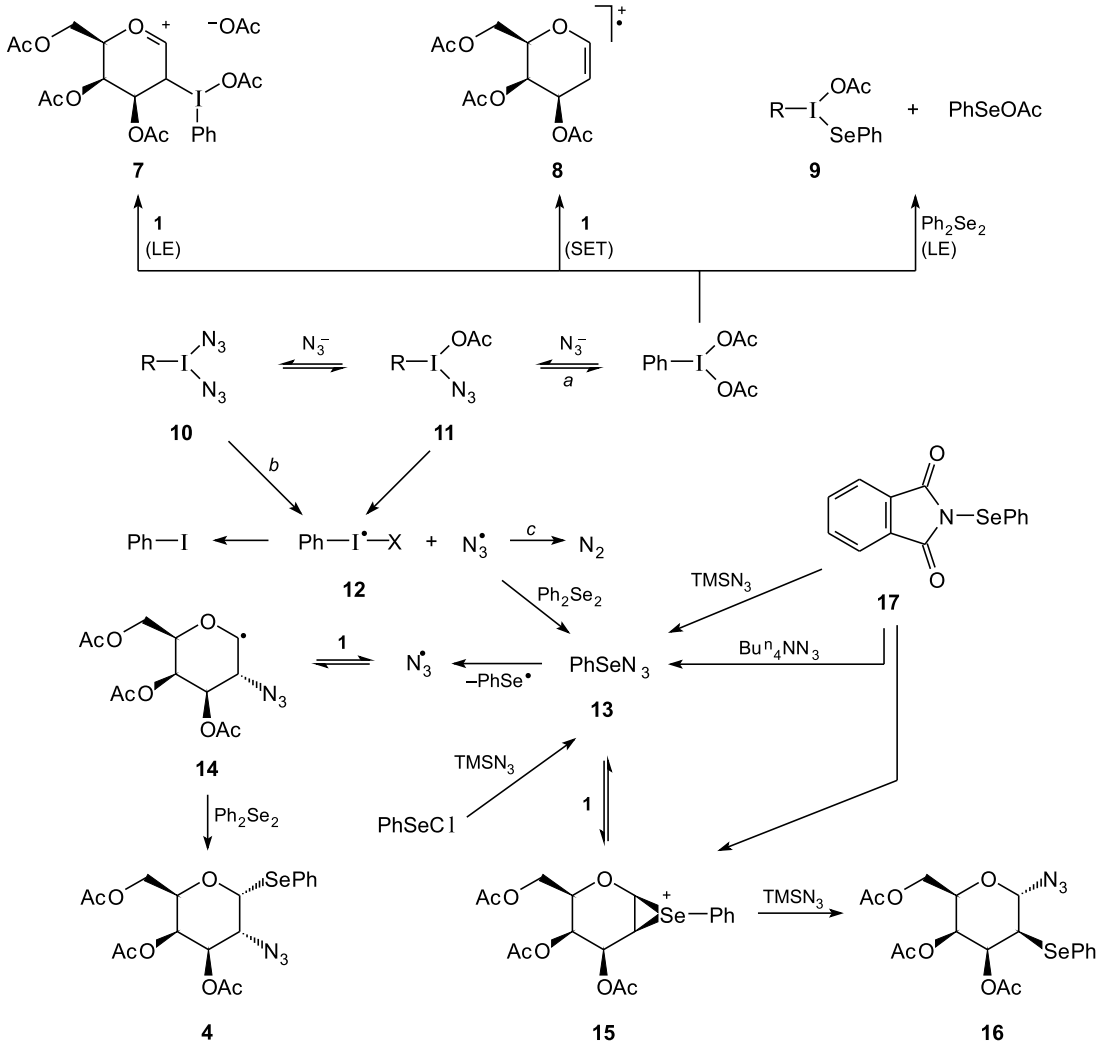


(*a*) Ligand exchange (LE); (*b*) LE, Nu is an arene;
(*b*′) single-electron transfer (SET);
(*c*) oxidative elimination

Note first that attempted direct replacement of diphenyl diselenide by an alkyl- or arylthio group source, including diaryl disulfides R_2S_2 (R = Ph, 4-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$, and 4-$O_2NC_6H_4$), dimethyl disulfide Me_2S_2, or various sulfides (TrSPh, $PhSO_2SPh$, and TMSSPh) failed under the conditions proposed[10] for the APS reaction ($TMSN_3$, $PhI(OAc)_2$, Ph_2Se_2, CH_2Cl_2, −10 °C). In all the above reactions, diacetoxyiodobenzene was reduced to iodobenzene without the formation of the corresponding thioglycosides, the starting glycal being intact. Therefore, these reactions do not produce a C radical (similar to intermediate **5** in Scheme 2), which could be expected to react with the aforementioned organosulfur compounds. (It is known that disulfides react with C radicals to give the corresponding sulfides.[14]) We assumed that the APS reaction mechanism differs from that proposed by Tingoli and does not involve the formation of a C radical as an initial reaction step.

The detection of intermediates **7**—**9** in the reaction mixture (see Scheme 4) could be evidence for a non-Tingolian mechanism of the APS reaction. However, presumed intermediates **7**—**9** were not detected directly by spectroscopic techniques (NMR or ESR). The NMR spectra of the reaction mixtures showed signals only for the starting reagents and the final products (iodobenzene and trimethylsilyl acetate) and no signals for iodine(III) compounds other than diacetoxyiodobenzene. The ESR spectra contained no signals for radicals even when we used the iodine(III) derivative $PhIPy_2(OTf)_2$. In the presence of this oxidant, which is superior to diacetoxy-

Scheme 4



N_3^- = $TMSN_3$, $TESN_3$, $TBDMSN_3$, $Bu^n_4NN_3$, NaN_3; X = N_3, OAc

iodobenzene, the generation of radical cations should be more probable.

Replacement of trimethylsilyl azide (azide anion donor) by Bu^n_4NF (fluoride anion donor) (F^- is a nucleophile unable to generate radicals in oxidative elimination) did not result in the formation of any products from glycal **1**, in particular, 2-deoxy-2-fluoro-1-phenylselenoglycoside (see Scheme 3, pathway *c*). Nor did the use of trimethylsilyl chloroacetate, which generates no radicals under mild conditions, initiate the addition to the double bond of the glycal. These examples demonstrate that the oxidative elimination of ligands in the coordination sphere of iodine (see Scheme 3, pathway *c*) is an important step in the APS reaction.

Based on the oxidation rate of diphenyl diselenide, we considered intermediate **9** to be incapable of participating in the APS reaction. For instance, no reaction occurred when triacetylgalactal **1**, trimethylsilyl azide, and diphenyl diselenide were mixed in the absence of diacetoxyiodobenzene at −10 °C. According to our and literature data,[15] the rate of room-temperature oxidation of diphenyl diselenide with diacetoxyiodobenzene is much lower than the APS reaction rate. For instance, ^{77}Se NMR monitoring of the reaction course revealed that a new signal at δ 1223 due[16] to a possible product containing the cationic fragment $PhSe^+$ accumulates in 1 day, while the APS reaction is completed in 4 h. Therefore, it is highly improbable that intermediate **9** can participate in the APS reaction.

Based on the results obtained, we returned to the assumption that azidophenylselenylation most likely starts with replacement of the acetoxy ligand in diacetoxyiodobenzene, which yields azidoiodinanes **10** or **11** (see Scheme 3, pathway *a*; see Scheme 4, step *a*). Then these compounds decompose to give azide radicals. This process is well known for azidoiodinanes;[17] they have been used as an azide radical source in azidation reactions,

while their thermolysis in the absence of radical acceptors produces molecular nitrogen.

The presence of the azide radical in the reaction mixture could be indirect evidence for the radical mechanism of the APS reaction. However, an ESR study of the reaction mixture did not detect azide radical intermediates, probably because of their very short lifetimes on the ESR time scale. To confirm the generation of the azide radical in the reaction mixture, we employed the spin trap technique[18] with nitrones **18** and **19** and nitroso compounds **20** and **21** as spin traps (Scheme 5). The ESR spectrum of adduct **22** obtained by a reaction of *N-tert*-butylphenylnitrone **18** with the azide radical is shown in Fig. 1 as an example. Structure **22** was determined by comparing its ESR spectrum with the literature data.[19] The splitting pattern and constants (a_N = 14.9, a_{H_β} = 1.9, and a_{N_β} = 1.9) agree with the published data[19] for its solution in acetonitrile.

At the same time, no other radical species were detected in the reaction mixture, probably because of full inhibition of the APS reaction in the presence of the nitrone and/or its adduct with the azide radical. We found that the stable nitroxyl radical TEMPO (**23**), which is similar to adduct **22**, also substantially lowers the APS reaction rate of galactal **1**, although the catalytic effect of TEMPO has been reported for related bisazidation reactions of simple enols (according to Ref. 20, the decomposition of azidoiodinanes **10** and **11** is promoted by TEMPO).

To follow the transformation pathways of the azide radical in the APS reaction, we studied model reactions of glycal **1** with $PhI(OAc)_2$—$TMSN_3$, $PhI(OAc)_2$—$Bu^n_4NN_3$, and PhIO—$TMSN_3$ in the presence or in the absence of

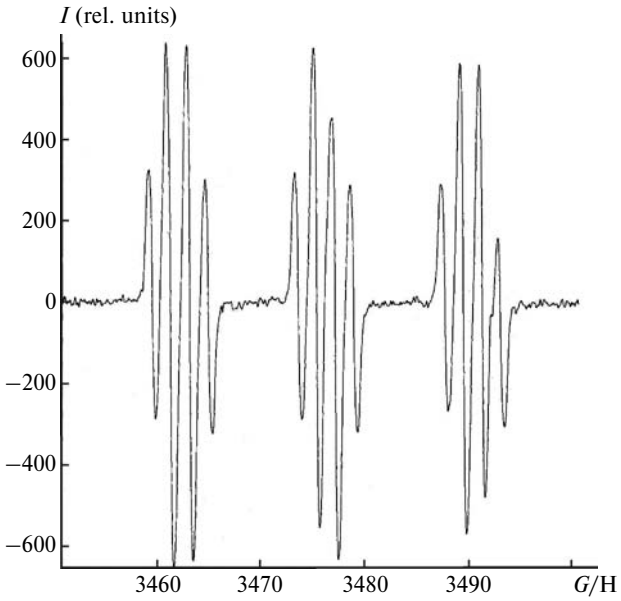
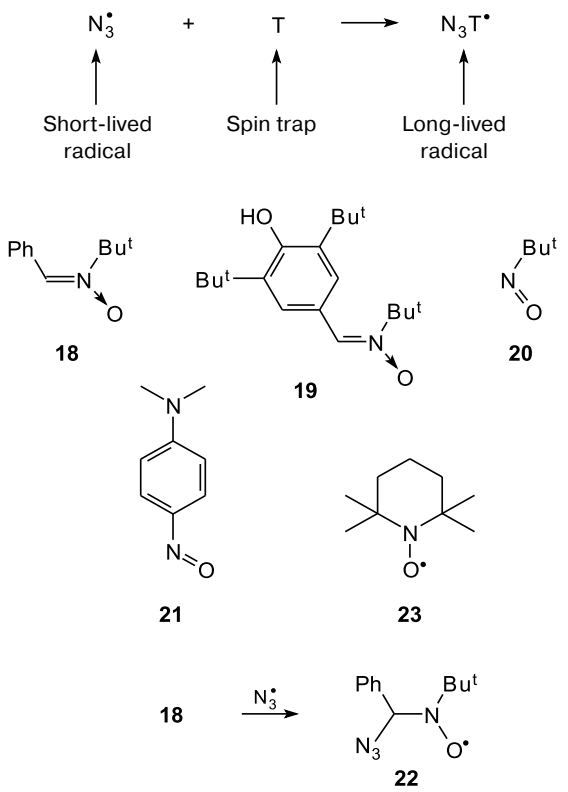


Рис. 1. ESR spectrum of adduct **22**.

Scheme 5



diphenyl diselenide by ^1H and ^{77}Se NMR spectroscopy. The above systems are characterized by different exchange rates of the ligands at the iodine atom (see Scheme 4, step *a*) and, consequently, by different rates of the overall process. Experiments were carried out in NMR tubes. The ligand exchange rate was estimated from the decreasing signal intensities for the starting reagents $PhI(OAc)_2$ and PhIO and the increasing signal intensities for PhI. The composition of each reaction mixture was analyzed by ^{77}Se NMR spectroscopy.

In a reaction of $PhI(OAc)_2$ with $TMSN_3$, diacetoxyiodobenzene and iodobenzene were identified only (^1H NMR data), while azidoiodinanes **10** or **11** were not detected (by analogy with chloroiodinanes, their spectra should differ from those of diacetoxyiodobenzene and iodobenzene[20]). Therefore, the rate of the decomposition of the azidoiodinanes to the azide radical is appreciably higher than the ligand exchange rate (see Scheme 4, step *b*). However, the data obtained are insufficient for pointing at the particular step in which the azide radical is generated: the formation of mixed iodinane **11** or diazidoiodinane **10**. A reaction of $PhI(OAc)_2$ with $TMSN_3$ and Ph_2Se_2 gives no other products but iodobenzene and trimethylsilyl acetate.

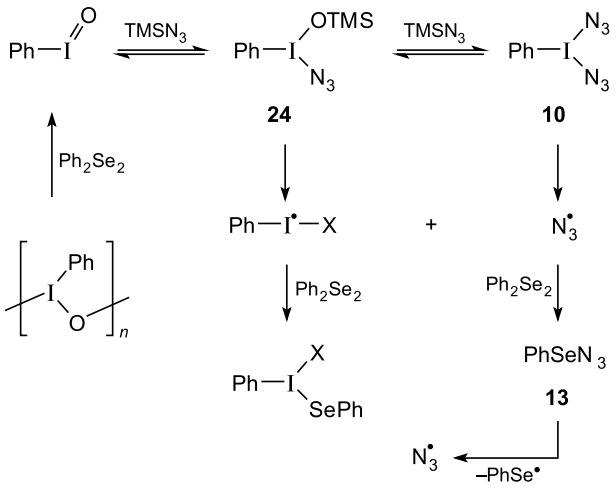
To clarify the mechanism of the APS reaction, we also carried out a reaction of triacetylgalactal **1** with a mixture of diacetoxyiodobenzene, diphenyl diselenide,

and tetrabutylammonium azide instead of trimethylsilyl azide. This reaction was not completed; the initial consumption rate of the starting reagent **1** (its conversion up to ~30%, monitoring by TLC) was much lower than that in the presence of trimethylsilyl azide. Then the reaction rate became comparable and again decreased at > 70% conversion of compound **1**. This kinetic profile can be explained by the fact that $Bu^n_4NN_3$ is much more reactive than $TMSN_3$ in nucleophilic substitution reactions. At the first step, when the concentration of the azide anion is high, the exchange rate of the acetoxy ligand is much higher than that in the presence of $TMSN_3$. As a result, the concentration of azide radicals becomes so high that the dominant process is their recombination rather than the addition to the alkene. At the final step, the high concentration of the resulting Bu^n_4NOAc suppresses the equilibrium ligand exchange, thus lowering the overall reaction rate.

Our study of the influence of the substituent nature in silyl azide on the APS reaction revealed a noticeable increase in the reaction time (up to several days versus four hours in the case of trimethylsilyl azide) for silyl azides with bulkier substituents (Et_3SiN_3 and $Bu^tMe_2SiN_3$). Thus, various azide anion sources affect only the exchange rate of the ligands in the coordination sphere of iodine(III) (*i.e.*, the rate of formation of azidoiodinanes, which seems to be the key step of the APS reaction).

With PhIO as an oxidant, the reaction rate depends strongly on the order of mixing of the reagents (Scheme 6). Addition of diphenyl diselenide to iodosobenzene resulted in immediate dissolution of the latter, which was not observed when diphenyl diselenide was added to a mixture of iodosobenzene and trimethylsilyl azide. According to NMR data, this reaction produces two new selenium compounds in which the Se atom bears an electron-withdrawing group. One of them is phenylselenyl azide **13** identified from the ^{77}Se NMR chemical shift (δ 1130).[21] Compound **13** was not isolated in the individual state because of its room-temperature decomposition into diphenyl diselenide and molecular nitrogen *via* recombination of the *in situ* generated radicals $N_3^\bullet$ (see Scheme 4, step *c*) and $PhSe^\bullet$. Thus, the generation of phenylselenyl azide from diphenyl diselenide and the azide radical (see Scheme 4, step *d*) and the reverse process are both possible at different steps of the APS reaction. It should be noted that thiocyanation of alkenes with a similar mixture of reagents (TMSCNS, $PhI(OAc)_2$, Ph_2Se_2, and CH_2Cl_2) gives phenylselenyl thiocyanate PhSeSCN, which is more stable (m.p. 49 °C) than phenylselenyl azide **13**.[22]

Scheme 6



X = N_3, OTMS

Our particular attention was given to the possibility of generating the azide radical from phenylselenyl azide **13**. Initially, we used phenylselenyl chloride as the starting material for the synthesis of phenylselenyl azide. However, the replacement of the chloride anion by azide at −10 °C cannot be effectively monitored by ^{77}Se NMR spectroscopy because of the very low intensity of the signal for selenium in phenylselenyl chloride at its concentration in the reaction mixture. An APS reaction of galactal **1** in the presence of phenylselenyl chloride and trimethylsilyl azide gives numerous products as a result of the opening of episelenonium intermediates of the type **15** (see Scheme 4) and only trace amounts of the target adduct **4**. This made the aforementioned method unsuitable for preparative synthesis of 2-azido-2-deoxyselenoglycoside derivatives.

For this reason, we used in subsequent experiments *N*-phenylselenophthalimide **17** as a source of the phenylselenyl group (see Scheme 4) because the phthalimide anion is known[22] to be virtually inert toward episelenonium cations. Trimethylsilyl azide and tetrabutylammonium azide were employed as azide anion sources in reactions with galactal **1**. Earlier,[23] a similar azidophenylselenylation process has been described for the system *N*-phenylselenophthalimide—$TMSN_3$—Bu^n_4NF in dichloromethane. Obviously, $TMSN_3$ in the presence of Bu^n_4NF promptly forms $Bu^n_4NN_3$, which further reacts with selenophthalimide.

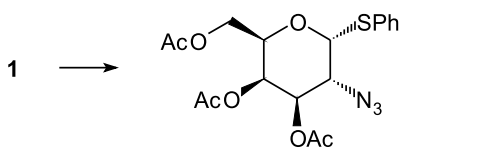
When trimethylsilyl azide is used, the reaction mixture contains a considerable amount of the ionic addition product **18**, probably because the generation rate of phenylselenyl azide is lower than the rate of formation of intermediate **16**. With much more nucleophilic $Bu^n_4NN_3$, phenylselenyl azide is generated rapidly and the dominant radical addition leads to product **4**. These results are in good agreement with the literature data.[23]

Based on the results obtained as a whole, we assumed that diphenyl diselenide in the APS reaction acts as both a scavenger of C radicals and a "preservative agent" for azide radicals during the formation and decomposition of phenylselenyl azide **14**, which inhibits removal of azide radicals as gaseous nitrogen from the reaction zone and,

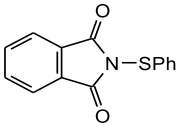
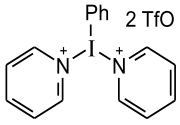
consequently, increases their lifetime in the reaction mixture.

Higher formation and decomposition temperatures could be expected for phenylsulfenyl azides as compared to phenylselenyl azide (−10 °C). Indeed, a room-temperature reaction gives thioglycoside **25** (see Ref. 24) in high yield with respect to the consumed galactal **1** (Scheme 7). A similar result was obtained with the iodine(III) derivative $Py_2I(OTf)_2$,[25] which sufficiently rapidly oxidizes diphenyl disulfide to PhS^+ and hence can also generate phenylselenyl azide *in situ*. The scope of synthetic application of both versions of single-step azidophenylsulfenylation with the systems **26**—$TBAN_3$ and **27**—Ph_2S_2 (see Scheme 7) will be a subject of further investigations.

Scheme 7



25

Reagents and conditions:  (**26**), $Bu^n_4NN_3$, CH_2Cl_2 or  (**27**), Ph_2S_2, $TMSN_3$, CH_2Cl_2

To sum up, we demonstrated that azidophenylselenylation most likely involves initial formation of azidoiodinanes **10** and/or **11** followed by their decomposition with generation of azide radicals. We also understood better the role of diphenyl diselenide and the ways of formation and transformation of phenylselenyl azide and other reaction intermediates and proposed the conditions for the single-step synthesis of thioglycosides from glycals *via* azidophenylsulfenylation as a novel reaction.

Experimental

Fluka, Acros, and Merck chemicals were used. Methods for purification of solvents and reagents, as well as conditions for NMR experiments and physicochemical constant determination, are described in Ref. 23. All 2D correlation spectroscopic experiments were carried out as recommended by the Bruker standard procedures. Optical rotation was measured for solutions in chloroform (*c* 1.0) on a PU-07 digital polarimeter at 19—21 °C. Thin-layer chromatography was carried out on Kieselgel-60 plates (Merck); spots were visualized by spraying 10 % (v/v) H_3PO_4 in ethanol and heating to ~150 °C. For column chromatography, Kieselgel-60 silica gel (Merck, 230—400 mesh) was used. Melting points were determined on a Kofler microunit. ESR spectra were recorded on a Bruker ER 200D—SRC spectrometer fitted with an ER 4105DR double resonator (9.5 GHz) with an ER 4111 VT thermocontroller and on a Bruker EMX 6/1 spectrometer fitted with an ER41O2ST resonator (9.8 GHz); *g* factors were determined with diphenylpicrylhydrazide as a standard. A weighed sample of a test compound (2—3 mg) was placed in an ESR tube and an anhydrous solvent (toluene or dichloromethane, 0.3 mL) was added. The tube was deaerated on an ultrasonic bath and $TMSN_3$ (5 μL) was added. NMR spectra were recorded on Bruker WM-250, Bruker AM-300, and Bruker DRX-500 instruments. A weighed sample of a test compound (0.1 mmol) was placed in an NMR tube and anhydrous dichloromethane (0.5 mL) was added.

Azidophenylselenylation (general procedure). A hypervalent iodine source (1.0 equiv.) and an azide anion source (2.0 equiv.) were added at −10 °C to a solution of triacetylgalactal **1** (1.0 equiv.) and diphenyl diselenide (1.0 equiv.) in CH_2Cl_2. The reaction mixture was stirred until the starting galactal was consumed completely (monitoring by TLC), concentrated, and analyzed using NMR spectroscopy.

3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-1-phenylseleno-α-D-galactopyranoside (4). ***A.*** Reaction with triethylsilyl azide. Diacetoxyiodobenzene (33 mg, 0.11 mmol) and then triethylsilyl azide (32 mg, 0.11 mmol) were added at −10 °C to a solution of galactal **1** (27 mg, 0.1 mmol) and diphenyl diselenide (32 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL). After 16-h stirring at −10 °C, the reaction mixture contained no starting galactal **1**.

B. Reaction with *tert*-butyl(dimethyl)silyl azide. Diacetoxyiodobenzene (38 mg, 0.12 mmol) and then *tert*-butyl(dimethyl)-silyl azide (39 mg, 0.12 mmol) were added at −10 °C to a solution of galactal **1** (31 mg, 0.11 mmol) and diphenyl diselenide (35 mg, 0.11 mmol) in CH_2Cl_2 (0.5 mL). After 56-h stirring at −10 °C, the reaction mixture contained no starting galactal **1**.

3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-1-phenylthio-α-D-galactopyranoside (25). ***A.*** A solution of tetrabutylammonium azide (60 mg, 0.21 mmol) was added dropwise for 1 h to a vigorously stirred solution of triacetylgalactal **1** (27.2 mg, 0.1 mmol) and *N*-phenylthiophthalimide **26** (51.1 mg, 0.2 mmol) in CH_2Cl_2 (0.5 mL). The reaction mixture was concentrated and the residue was chromatographed on silica gel with gradient elution from toluene to ethyl acetate. The yield of adduct **25** was 24.5 mg (51%). The starting galactal (12.5 mg) was partially recovered. The NMR spectra of compound **25** agree with the literature data.

B. A solution of tetrabutylammonium azide (60 mg, 0.22 mmol) was added dropwise for 1 h to a vigorously stirred solution of triacetylgalactal **1** (29.3 mg, 0.108 mmol), diphenyl disulfide (46.9 mg, 0.2 mmol), and compound **27** (135 mg, 0.21 mmol) in CH_2Cl_2 (1.0 mL). The reaction mixture was concentrated and the residue was chromatographed on silica gel with gradient elution from toluene to ethyl acetate. The yield of adduct **25** was 17 mg (33%). The starting galactal (13.3 mg) was partially recovered. The NMR spectra of compound **25** agree with the literature data.

3,4,6-Tri-*O*-acetyl-1-azido-2-deoxy-2-phenylseleno-α-D-galactopyranoside (16). Sodium azide (435 mg, 6.60 mmol) and

diacetoxyiodobenzene (298 mg, 0.91 mmol) were added to a solution of triacetylgalactal **1** (120.9 mg, 0.44 mmol) in DMF (3 mL). The reaction was accompanied by vigorous gas evolution. The suspension was stirred until the starting galactal was consumed completely (120 h), diluted with CH_2Cl_2, and poured into a saturated solution of $NaHCO_3$. The organic layer was separated. The aqueous layer was washed three times with CH_2Cl_2. The combined organic layers were filtered through cotton and evaporated to dryness. The residue was separated by column chromatography in toluene—ethyl acetate to give compound **16** (94 mg, 45%), R_f 0.39 (toluene—ethyl acetate, 5 : 1), $[\alpha]_D$ +9.5 (*c* 1.0, EtOAc). Further elution gave compound **4** (101 mg, 47%). ^{1}H NMR ($CDCl_3$), δ: 7.50—7.60 (m, 2 H, Ar); 7.30—7.40 (m, 3 H, Ar); 2.23, 2.11, 2.08 (all s, 9 H, Ac). ^{13}C NMR ($CDCl_3$), δ: 169.5—170.0 (C=O); 128.1—136.6 (Ar); 20.5—20.7 ($\underline{C}H_3C$=O). Found (%): C, 45.92; H, 4.57; N, 8.82; Se, 16.98. $C_{18}H_{21}N_3O_7Se$. Calculated (%): C, 45.97; H, 4.50; N, 8.93; Se, 16.79.

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