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Dihydropyranone Formation by *Ipso* C−H Activation in a Glucal 3-Carbamate-Derived Rhodium Acyl Nitrenoid

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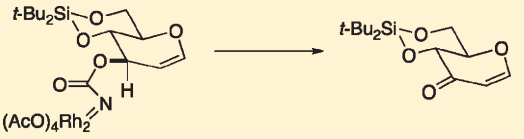
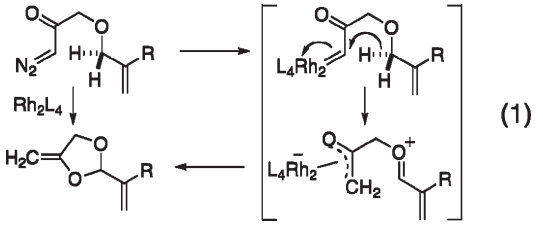
Supporting Information

ABSTRACT: By using (*N*-tosyloxy)-3-*O*-carbamoyl-D-glucal **10**, which removes the need for a hypervalent iodine(III) oxidant, we provide evidence for rhodium nitrenoid-mediated *ipso* C−H activation as the origin of a C3-oxidized dihydropyranone product **3**. This system may be especially susceptible to such a pathway because of the ease of forming a cation upon hydride transfer to the rhodium-complexed acyl nitrene.



In the C−H insertion chemistry of metal carbenoids (usually rhodium- but also copper- and ruthenium-stabilized), anomalous products can form when hydride transfer to the carbenoid results in a particularly well-stabilized cation.[1] For example, Clark and co-workers found acetal byproducts in dirhodium(II)-catalyzed reactions of certain α-diazoketones (eq 1).[1c,i] Mechanistic investigations led to the conclusion that hydride transfer, probably to the rhodium center but possibly to the carbenoid carbon (shown below), provided an oxocarbenium ion en route to the acetal. In the area of metallanitrene chemistry, meanwhile, there have been hints of related reactivity, but examples remain limited.[2] Herein, we report our investigations on a system that is apparently well set up for intramolecular hydride transfer to a rhodium acyl nitrenoid moiety.



(1)

During studies on the dirhodium(II)-catalyzed oxidative cyclization of D-glucal 3-carbamates to oxazolidinone-protected 2-aminoglycosides (e.g., **1**→**2**), we discovered concurrent formation of C3-oxidized dihydropyranones such as **3**.[3] Our mechanistic hypothesis[3b] was that **2** and **3** both stemmed from a common acyl nitrenoid intermediate (**5**), which could undergo either alkene insertion or C3-H oxidation (Scheme 1). However, the use of an iodine(III) oxidant[4] in conjunction with the known Lewis acidic properties of Rh(II) carboxylates[5] left open the possibility that **2**, **3**, or both might be forming via initial reaction of the hypervalent iodine species at the enol ether π bond. In this paper, we provide evidence, including examples where **2** and **3** arise from a pre-N-oxidized substrate in the absence of iodine(III), that both the amino sugar (**2**) and C3-oxidation (**3**) products come from rhodium-complexed nitrene **5**, and we discuss the formation of **3** by analogy to Clark's hypothesis (eq 1).

Our motivation to investigate the origin of **3** under our reaction conditions was reinforced by Kirschning's thorough studies[4a−c] on dihydropyranone formation from glycals by hydroxytosyloxyiodobenzene (Koser's reagent[6]). This process, which transforms a variety of 3*O*-protected glycals, including tri-*O*-acetyl-D-glucal **6**, entails initial addition of the iodine(III) oxidant at the glycal alkene. While Koser's reagent is considerably more reactive than the iodosobenzene used in our reactions, a Kirschning-type route to the **3** formed under our conditions, perhaps with Lewis acid activation of PhIO by dirhodium(II)acetate, was a viable mechanistic option (Scheme 2).[7] Furthermore, it was possible that **2** could also form through initial olefin activation by the iodine(III) oxidant, followed by cyclization of the carbamate nitrogen and glycosylation.

Initially, we engineered a series of control experiments to examine these options. Neither **2** nor **3** formed from glucal 3-carbamate **1** in the absence of rhodium.[8] We also subjected noncarbamate glycals **6** and **7a**,**b**[9] (Figure 1) to our conditions but observed no dihydropyranone formation, even though substrate **7a** contained a 3*O*-silyl ether, making it particularly prone to Kirschning's oxidation.[4a] Furthermore, there was no sign of oxidative cyclization or C3−H oxidation when we tested glucal- or allal-derived *N*-tosyl or *N*-phenyl carbamates **7c**−**e**.[9]

In an alkene activation mechanism, the $Rh_2(OAc)_4$ catalyst would act as a Lewis acid to increase the electrophilicity of the iodine(III) center.[4d,e,10] Were this the case, other Lewis acids, despite lacking the nitrene-stabilizing capacity of dirhodium(II), should also promote formation of **2** and **3**. To the contrary, a number of Lewis acids [$Zn(OTf)_2$, $Sm(OTf)_3$, $La(OTf)_3$] failed to catalyze the reaction of **1**.

Since the control experiments indicated that **2** and **3** do not arise through initial C=C activation by the iodine(III) species,

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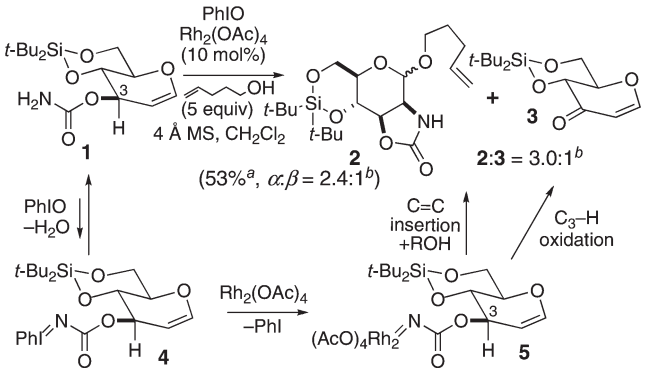
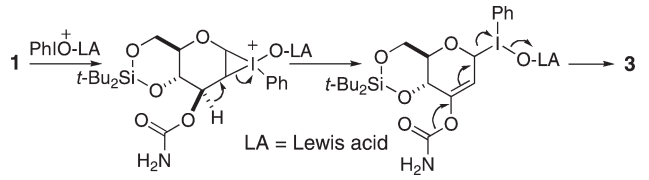
Scheme 1. Amidoglycosylation and C3 Carbonyl Formation from an Acyl Nitrenoid Intermediate



[a] Combined yield of both anomers after silica gel chromatography. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. Ratios are the average of five experiments.

Scheme 2. Possible Route to Dihydropyranone 3 via Reaction of the Glycal Alkene with the Iodine(III) Oxidant



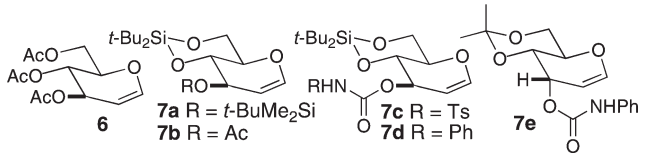
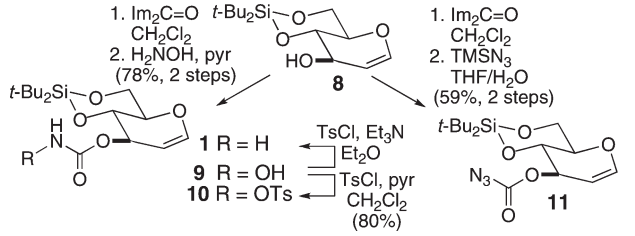


Figure 1. Control compounds that gave neither dihydropyranone formation nor oxidative cyclization under the amidoglycosylation conditions [PhIO (1.8 equiv), $Rh_2(OAc)_4$ (0.1 equiv), 4-penten-1-ol (5 equiv), 4 Å MS, CH_2Cl_2].

we next sought to probe whether **2** and **3** form when a rhodium-complexed nitrene **5** is generated in the absence of any iodine(III) oxidant. The means to conduct such a test came from Lebel and co-workers who have used *N*-tosyloxycarbamates as a pre-oxidized nitrogen atom source for dirhodium(II)-catalyzed C−H and C=C insertions.[11] Both the Fleming and Lebel groups have demonstrated copper-catalyzed variants,[12] and Donohoe has applied a similar strategy, using *N*-acyloxycarbamates in osmium-catalyzed tethered aminohydroxylations.[13]

We prepared what turned out to be a sensitive *N*-tosyloxy glucal 3-carbamate **10** from silylene-protected alcohol **8**[9a] (Scheme 3). The intermediate *N*-hydroxycarbamate **9** was a stable solid. However, attempted tosylation under Lebel's and Fleming's conditions (TsCl, Et_3N, Et_2O) provided a complex mixture, from which we isolated primary carbamate **1** as the principal component. Evidently, as the desired *N*-tosyloxycarbamate **10** formed, it underwent base-induced, metal-free nitrene formation and subsequent hydrogen atom abstraction.[11c,14] Using an alternative procedure (TsCl, pyr, CH_2Cl_2), however, provided clean conversion to the desired **10**. This material could be purified by

Scheme 3. Preparation of *N*-Tosyloxy Glucal 3-Carbamate 10 and 3-Azidoformate 11



chromatography on silica gel, but attempts to store it neat, even at −20 °C, resulted in decomposition to a black tar, probably indicating formation of *O*-*p*-toluenesulfonylhydroxylamine[15] upon decarboxylative loss of the C3 substituent. Nevertheless, **10** was tractable when freshly prepared, purified by chromatography, and used promptly in CH_2Cl_2 solution.

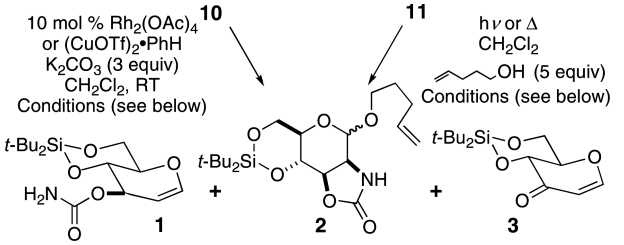
Upon treatment with dirhodium(II)acetate[16] and K_2CO_3 in CH_2Cl_2, *N*-tosyloxy glucal 3-carbamate **10** gave a complex reaction mixture, from which we identified dihydropyranone **3** and primary carbamate **1** by comparison with authentic samples (Table 1, entry 1). This shows that the C3 carbonyl of **3** can form from an acyl nitrenoid precursor under conditions where the Kirschning-type mechanism is impossible. The production of **1** under these conditions may occur via the nitrene by hydrogen atom abstraction. Lebel has observed analogous products in reactions of other *N*-arylsulfonyloxycarbamates.[11c] In the absence of dirhodium(II), decomposition of the starting material **10** occurred, but neither **1** nor **3** was detected by ^{1}H NMR analysis of the reaction mixture.[17]

Dirhodium(II)acetate-catalyzed reaction of **10** in the presence of 4-penten-1-ol as a nucleophile provided α and β amidoglycosylation products **2**, dihydropyranone **3**, and primary carbamate **1** (Table 1, entry 2). The ratio of amidoglycosylation to dihydropyranone formation (**2**:**3**) and the α:β ratio of **2** were similar to the results using the primary carbamate **1** with iodosobenzene oxidant (cf. Scheme 1).[18] This is further evidence that both the iodine(III)-mediated process with **1** and the reaction starting from pre-N-oxidized substrate **10** proceed through the same intermediate, the rhodium acyl nitrenoid **5**, which partitions between C=C insertion and C3−H activation. Control experiments including **10** and 4-penten-1-ol, but omitting either the $Rh_2(OAc)_4$ or the inorganic base, consumed the *N*-tosyloxycarbamate but did not lead to detectable formation of products **1**, **2**, or **3**.[17] Separately, we verified that a sample of dihydropyranone **3**, prepared by PDC oxidation of allylic alcohol **8**, was stable to the combination of $Rh_2(OAc)_4$ and K_2CO_3 in CD_2Cl_2, either in the absence or presence of 4-penten-1-ol.

We obtained similar results (Table 1, entry 3), including formation of dihydropyranone **3**, with the copper catalyst used in Fleming's study,[12a] suggesting that the analogy between carbenoid and nitrenoid chemistry extends both to rhodium and copper catalysis. Indeed, copper carbenoid reactions corresponding to the process in eq 1 are known.[1k−m]

Finally, we prepared glucal 3-azidoformate **11** (Scheme 3) via the acyl imidazole under aqueous conditions[19] and investigated it as a nitrene source. Photolysis without or with $Rh_2(OAc)_4$ (Table 1, entries 4 and 5) gave the amidoglycosylation product **2**, but no trace of **3**.[20] The thermal reactions led only to very limited amounts of products **1**−**3**.[21] The catalyst-free thermal reaction

Table 1. Results Using 10 and 11 as Metal Nitrenoid or Nitrene Precursors



Entry	SM	Conditions	%**1**[a]	%**2** (α:β)[a]	%**3**[a]
1	**10**	No added alcohol $Rh_2(OAc)_4$	10[b]	N/A	11[b] (**3**:**1** = 1.1:1[b])
2	**10**	OH (5 equiv) $Rh_2(OAc)_4$	10[b]	35[b] (3.0:1[b])	13[b] (**2**:**3** = 2.8:1[b])
3	**10**	OH (5 equiv) $(CuOTf)_2$•PhH	12	30 (2.4:1)	6
4	**11**	hν[c]	-*d*-	44 (1.5:1)	None
5	**11**	hν[c], $Rh_2(OAc)_4$	-*d*-	20 (2.4:1)	None
6	**11**	100 °C	None	2 of β[e]	None
7	**11**	100 °C, $Rh_2(OAc)_4$	5	8 (3.0)	2

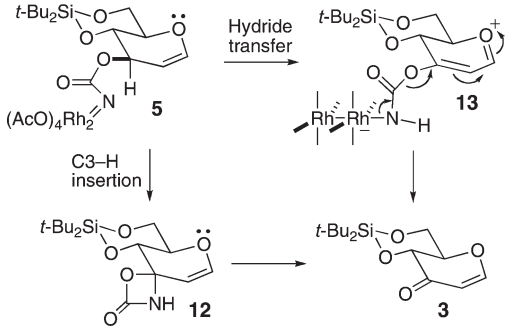
[a] Yields and anomeric ratios determined by ^{1}H NMR analysis of the crude reaction mixture with mesitylene as an internal standard. [b] The reported value is the average of three experiments. [c] 254 nm, Vycor filter. [d] Not detected, but regions in ^{1}H NMR spectra of the crude reaction mixture that would have contained resonances for **1** were obscured by other signals. [e] The α anomer was also detected by ^{1}H NMR analysis, but the α/β ratio could not be reliably determined due to overlapping signals.

(entry 6) gave none of the dihydropyranone **3**, while a detectable level of this material did form when $Rh_2(OAc)_4$ was included (entry 7). From our experiments with **11**, we conclude that the metal-free nitrene undergoes the amidoglycosylation process to **2**[14a] but does not provide C3-oxidized **3**. Also, the rhodium-complexed nitrene is not constituted photochemically but does arise to a small extent thermally, as suggested by formation of **3** in the reaction of entry 7.

The significance of the findings outlined in this paper lies in clarifying the origin of the *ipso*-oxidized **3** rather than from the synthetic utility of the process. In fact, the use of either *N*-tosyloxy glucal 3-carbamate **10** or azidoformate **11** is considerably less effective for the desired alkene insertion process than using primary carbamate **1** with iodosobenzene and $Rh_2(OAc)_4$ as depicted in Scheme 1.

While our results do not provide detailed information about the nitrene-mediated C3−H oxidation process, possibilities include C−H insertion followed by fragmentation of the resulting four-membered-ring carbamate **12** (Scheme 4), as suggested in the work of Du Bois.[2a,b] Alternatively, particularly in **5** where the C3−H bond is vinylogously anomeric and favorably aligned with the enol ether π system, the oxidation may involve hydride transfer (**5**→**13**), leading to the resonance-stabilized cationic portion of zwitterion **13**. Given the analogous processes previously identified for dirhodium(II) carbenoids,[1] hydride transfer to the acyl carbonyl, to the rhodium center, or directly to nitrogen (as shown in Scheme 4) are all viable alternatives. Consistent with hydride migration from C3 to the metallanitrene, we have recently reported that dihydropyranone formation is suppressed by

Scheme 4. Proposed Formation of 3 by Hydride Transfer or C−H Insertion from the Rhodium Acyl Nitrene



inductive and conformational factors when the 4*O* and 6*O* protecting groups are electron-withdrawing.[3b]

In conclusion, this study presents evidence that rhodium acyloxy nitrenoids can undergo *ipso* carbonyl formation. Certain glycal 3-carbamate substrates are particularly prone to this pathway because of the electron-rich character of the C3−H bond and the stability of the resulting vinylogous oxocarbenium ion. A better understanding of mechanism will aid efforts to improve the chemoselectivity of nitrenoid C=C and C−H insertion processes.

EXPERIMENTAL SECTION

4,6-*O*-Di-*tert*-butylsilylene-3-*O*-(*N*-hydroxycarbamoyl)-D-glucal (9). To a solution of alcohol **8**[9a] (0.501 g, 1.75 mmol) in CH_2Cl_2 (20 mL) was added 1,1′-carbonyldiimidazole (0.425 g, 2.62 mmol). After 2 h at room temperature, the mixture was diluted with CH_2Cl_2 (80 mL) and washed with satd aq NH_4Cl (3 × 80 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated, providing the carbonyl imidazole intermediate as a light yellow foam. Without further purification, this material (assumed 1.75 mmol) was dissolved in pyridine (4.0 mL), and hydroxylamine hydrochloride (0.365 g, 5.25 mmol) was added. After being stirred for 60 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (80 mL) and washed with water (2 × 80 mL) and brine (80 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. The crude product was chromatographed (30% EtOAc/hexanes, 100 mL SiO_2), yielding *N*-hydroxycarbamate **9** as a white solid (0.470 g, 78%): mp 110.0 °C; R_f = 0.21 (30% EtOAc/hexanes); IR (thin film) 3315, 1731, 1649 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 1H), 6.92 (very br s, 1H), 6.33 (dd, J = 6.0, 1.5 Hz, 1H), 5.34 (dt, J = 7.5, 1.8 Hz, 1H), 4.80 (dd, J = 6.1, 2.1 Hz, 1H), 4.25−4.10 (m, 2H), 4.04−3.85 (m, 2H), 1.05 (s, 9H), 0.99 (s, 9H); ^{13}C NMR[22] (75 MHz, $CDCl_3$) δ 160.0 (s), 145.2 (o), 100.3 (o), 74.4 (o), 73.6 (o), 72.8 (o), 65.6 (t), 27.4 (o), 26.8 (o), 22.7 (s), 19.8 (s); HRMS (FAB) m/z calcd for $C_{15}H_{28}NO_6Si$ (M + H)$^+$ 346.1686, found 346.1688.

4,6-*O*-Di-*tert*-butylsilylene-3-*O*-(*N*-tosyloxycarbamoyl)-D-glucal (10). *N*-Hydroxycarbamate **9** (105 mg, 0.304 mmol) was dissolved in CH_2Cl_2 (1.5 mL), and pyridine (74 μL, 0.92 mmol) was added, followed by *p*-toluenesulfonyl chloride (89 mg, 0.47 mmol). The solution was stirred at 25 °C during 4.5 h, diluted with CH_2Cl_2 (25 mL), and washed with water (2 × 20 mL) and brine (1 × 20 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. The crude material was chromatographed immediately (20→25→30% EtOAc/hexanes, 50 mL of SiO_2). Because **10** was prone to decomposition when kept neat for extended periods of time, the yield was determined by weight after concentration on the rotovap, followed by 5 min on the

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vacuum line. The resulting product **10**, a colorless foam (~120 mg, 80%), consequently contained traces of solvent, and the reported yield is therefore approximate. After weighing, **10** was dissolved in CH_2Cl_2 (1.0 mL) and used immediately: R_f = 0.52 (30% EtOAc/hexanes); IR (thin film) 3281, 1775, 1736, 1647, 1597 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 8.20 (s, 1H), 7.86 (apparent d, J = 8.4 Hz, 2H), 7.37 (apparent d, J = 8.0 Hz, 2H), 6.31 (dd, J = 6.0, 1.4 Hz, 1H), 5.21 (dt, J = 7.4, 1.8 Hz, 1H), 4.53 (dd, J = 6.1, 2.0 Hz, 1H), 4.16 (dd, J = 9.6, 4.4 Hz, 1H), 4.03 (dd, J = 10.2, 7.4 Hz, 1H), 3.95 (t, J = 9.9 Hz, 1H), 3.87 (td, J = 10.1, 4.5 Hz, 1H), 2.45 (s, 3H), 1.05 (s, 9H), 0.96 (s, 9H); ^{13}C NMR[22] (75 MHz, CD_2Cl_2) δ 155.9 (s), 147.0 (s), 146.1 (o), 131.0 (s), 130.4 (o), 130.0 (o), 100.0 (o), 75.7 (o), 73.9 (o), 73.4 (o), 66.2 (t), 27.7 (o), 27.2 (o), 23.1 (s), 22.1 (o), 20.2 (s); HRMS (FAB) m/z calcd for $C_{22}H_{34}NO_8SiS$ $(M + H)^+$ 500.1774, found 500.1760.

Reaction of 10 Including 4-Penten-1-ol. Potassium carbonate (96 mg, 0.69 mmol) and $Rh_2(OAc)_4$ (11 mg, 0.025 mmol) were combined in a 10 mL round-bottom flask, and 4-penten-1-ol (125 μL, 1.23 mmol) was added, followed immediately by a solution of freshly prepared *N*-tosyloxycarbamate **10** (~114 mg, 0.228 mmol) in CH_2Cl_2 (1.0 mL). The carbamate-containing pear-shaped flask was rinsed with CH_2Cl_2 (2 × 1.0 mL) with the rinsings being added to the reaction mixture. The well-stirred mixture turned from a blue-green-gray to a purple color within 20−30 min. Stirring was continued for 16 h, and the purple mixture was filtered through a tightly packed pad of Celite, rinsing with EtOAc (80 mL). The filtrate was concentrated and the crude material analyzed by ^1H NMR (separately in $CDCl_3$ and acetone-d_6), with comparison to authentic samples of **1**−**3**. The **2**:**3** and **2**-**α**:**2**-***β*** ratios were best measured in acetone-d_6 from the resonances for H3 of **2**-**α** (δ 4.56), H1 of **2**-***β*** (δ 4.86), and H2 of **3** (δ 5.33). The yields were determined by ^1H NMR analysis of the crude in $CDCl_3$ using the H1 signals for **2**-**α** and **2**-***β*** (δ 4.81 and δ 4.69, respectively), the H2 signal for **3** (δ 5.41), and the H3 signal for **1** (δ 5.27) versus mesitylene added as an internal standard. The reported ratios and yields are the averages from three separate runs.[23]

■ ASSOCIATED CONTENT

Supporting Information. Complete experimental details, including preparation and characterization of compounds **7a**−**e**, procedures for control experiments, and copies of ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The crude reaction mixtures were analyzed by ^{1}H NMR ($CDCl_3$ and/or acetone-d_6) and TLC with comparison to authentic samples of **1**−**3**. See the Supporting Information for details.

(18) Differences in the mean values for the **2**-**α**:**2**-***β*** and the **2**:**3** ratios for the reactions in Scheme 1 and Table 1, entry 2, are quite small but nevertheless statistically significant according to a Student's *t* test analysis (see the Supporting Information for details). We attribute this to the effect of the different reaction conditions (especially the presence of K_2CO_3 in reactions of **10**) on trapping of the intermediate glycosyl donor formed by C═C insertion of the acyl nitrenoid.

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(20) Control experiments showed that **3** degrades by about 60% in 1 h under the photolysis conditions. Because we used limited photolysis times and examined the reaction mixtures at partial conversion, we expect that **3** would have been detected had it formed during photolysis of **11**. See the Supporting Information for complete experimental details.

(21) The main product was allylic substitution by 4-penten-1-ol at C1 upon loss of the $-OC(O)N_3$ group from C3.

(22) ^{13}C NMR peak multiplicities were inferred via DEPT 135 measurements. The label "o" (for odd number of attached hydrogens) denotes a CH or CH_3, "s" denotes a carbon with no attached hydrogens, and "t" denotes a CH_2.

(23) See the Supporting Information for standard deviations.