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A Visible-Light-Promoted *O*-Glycosylation with a Thioglycoside Donor

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Abstract: *Visible-light irradiation of 4-p-methoxyphenyl-3-butenylthioglucoside donors in the presence of Umemoto's reagent and alcohol acceptors serves as a mild approach to O-glycosylation. Visible-light photocatalysts are not required for activation, and alkyl- and arylthioglycosides not bearing the p-methoxystyrene are inert to these conditions. Experimental and computational evidence for an intervening electron donor–acceptor complex, which is necessary for reactivity, is provided. Yields with primary, secondary, and tertiary alcohol acceptors range from moderate to high. Complete β-selectivity can be attained through neighboring-group participation.*

Thioglycosides are among the most commonly used glycosyl donors for chemical *O*-glycosylation.[1] The ease of synthesis, straightforward handling, configurational stability, and tunable reactivity are among the positive attributes associated with this class of glycosyl donor. Thioglycosides have proven to be useful in the late-stage synthesis of glycans and in generating historically difficult glycosidic linkages.[1,2] The development of easily performed *O*-glycosylations[3] using thioglycosides and bench-stable reagents for high-yielding, stereoselective *O*-glycosylations at or near ambient temperature has been identified as a worthy (but lofty) goal. Progress has been made with the development of, among others, approaches using gold catalysis, iodine(III) reagents, and bismuth(V) reagents.[4]

By contrast, we and others have identified irradiation with light, especially visible light, as an intriguing approach to the activation of thio- and selenoglycosides under mild, user-friendly reaction conditions.[5] In this case, photons supply the energy needed for the activation of recalcitrant thioglycosides. The majority of photochemical glycosylations with chalcogenoglycoside donors likely involve photoinduced electron transfers which trigger the formation of S/Se-centered radical cations that fragment to the putative oxocarbenium intermediate. This approach has proven successful in one case with visible-light irradiation of *p*-methoxyphenylthioglycoside donors in the presence of an iridium photosensitizer.[5a] Though these initial results were encouraging, moderate yields with more difficult glycosidic linkages (a problem that plagues the entire field of photochemical glycosylation)[5] suggests that further work is needed to make visible-light *O*-glycosylation applicable to synthetically challenging targets.

While our own studies on visible-light photochemical *O*-glycosylation proved successful with phenylselenoglycosides,[5d] further investigations with electron-rich arylthioglycosides and some of the most strongly oxidizing visible-light photosensitizers[6] were unproductive. The formation of sulfur-centered thioglycoside radical cations is a nontrivial task under visible-light irradiation. As an alternative strategy, we imagined a scenario in which visible-light photocatalysis could be used to unburden the sulfur from an apparently difficult single-electron oxidation. Taking inspiration from the visible-light photocatalytic oxytrifluoromethylation of styrenes,[7] we envisioned an approach which would allow the use of stable thioglycosides and the facile photocatalytic generation of trifluoromethyl radicals.

We imagined that visible-light-promoted excitation of $[Ru(bpy)_3]^{2+}$ would precede single-electron transfer to Umemoto's reagent to generate a trifluoromethyl radical, dibenzothiophene, and $[Ru(bpy)_3]^{3+}$ (Scheme 1). Attack of the trifluoromethyl radical on the styrene portion of glycosyl donors, having the generic structure **1**, would result in the benzylic radical **2**, which could be oxidized by $[Ru(bpy)_3]^{3+}$ to generate the carbocation **3** and regenerate $[Ru(bpy)_3]^{2+}$.[7] Cyclization of sulfur onto the cation of **3** would result in the intermediate **4**, which we deemed competent as an activated donor for *O*-glycosylation. Such a process would provide a mild approach to *O*-glycosylation with a thioglycoside donor, which would have orthogonal reactivity to other thioglycoside donors. Like thioglycosides, $[Ru(bpy)_3]^{2+}$ salts and Umemoto's reagent are easily handled, bench-stable species. This approach could also prove useful for the iterative synthesis of oligosaccharides even in a one-pot milieu. While a mechanistically related approach has been reported with *O*-pentenylgycoside donors,[8a] this approach would avoid the use of molecular bromine and the intermediacy of moribund glycosyl bromides.[8b]

Herein, we report our results which were inspired by the hypothesis in Scheme 1. *O*-glycosylations proceed in moderate to high (44–93%) yields and complete β-selectivity can be afforded. The 4-*p*-methoxyphenyl-3-butenylthioglucosides studied here react under reaction conditions to which alkylthio- and arylthioglycosides are inert, thus supplying a novel approach to orthogonality with potential applications in oligosaccharide synthesis. We provide experimental and computational evidence for the intervention of an electron donor–acceptor (EDA) complex[9] which obviates photo-

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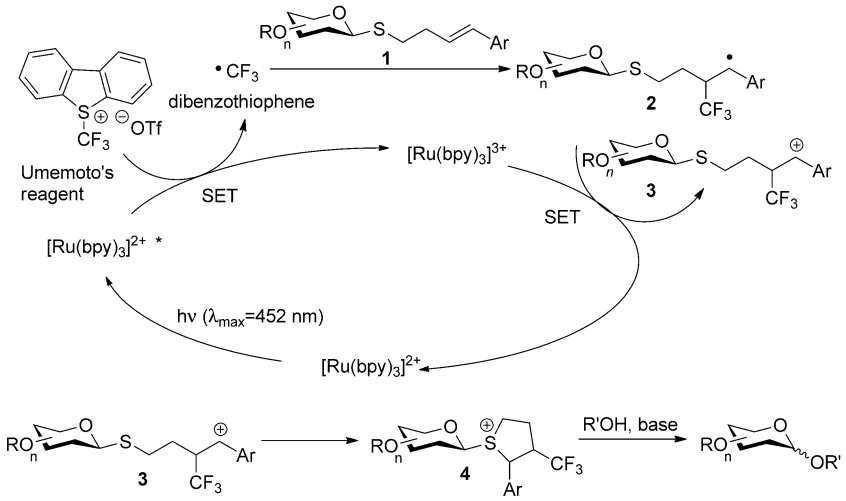


Scheme 1. Original hypothesis for visible-light-promoted *O*-glycosylation with thioglycosides. bpy = 2,2′-bipyridine, Tf = trifluoromethanesulfonyl.

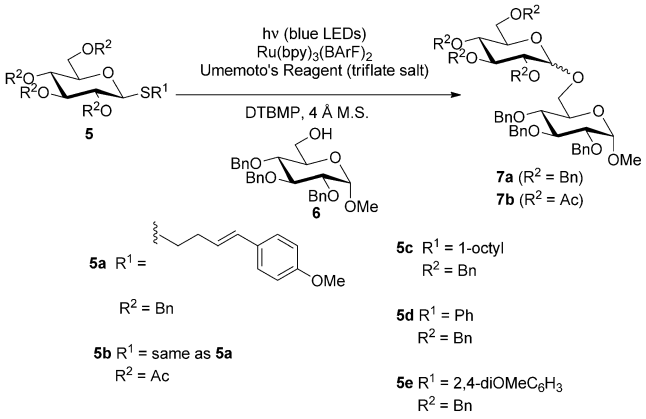
sensitizers like $[Ru(bpy)_3]^{2+}$. This reaction represents the first example of a visible-light-promoted glycosylation not requiring a photocatalyst/photosensitizer.

To test the hypothesis outlined in Scheme 1, we synthesized a series of thioglucosides (Table 1), including the benzyl-protected **5a**, acetyl-protected **5b**, and the aryl- and alkyl-thioglycosides **5c–e**.[10] We reasoned that an electron-rich styrene moiety would react more quickly with the electrophilic trifluoromethyl radical than an electron-neutral or electron-poor styrene.[11] Thus, we targeted the *para*-methoxyphenyl-bearing substrates **5a/b**. Our initial reaction conditions involved irradiation with blue LEDs ($\lambda_{max} = 455$ nm) in the presence of Umemoto's reagent, 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), and the acceptor **6** with 4 Å molecular sieves in CH_2Cl_2. In the event (entry 1), irradiation of one of these mixtures with the donor **5a** resulted in a 55% yield of the product **7a** as a mixture of anomers. A solvent screen demonstrated insignificant differences or inferior results from those obtained using CH_2Cl_2 (see the Supporting Information). Controls demonstrated that irradiation and Umemoto's reagent are essential (entries 2 and 3). However, irradiation without $[Ru(bpy)_3]^{2+}$ provided similar yields of **7a** (entry 4)! This surprising outcome is likely due to the formation of an EDA complex.[9] Further optimization showed that using **5a** in excess and increasing the concentration resulted in an increase in yield (entry 5). Increasing the concentration but using the acceptor **6** in excess, as in entries 1–4, did not improve yields (data not shown). In addition, omission of DTBMP (entry 6) provided comparable results to entry 5 while omission of DTBMP and molecular sieves resulted in complex mixtures and difficult purification (data not shown). Implementation of entry 6 conditions at −20 °C provided no improvement (see the Supporting Information).

The potential orthogonality of this method toward other thioglycosides intrigued us. Application of the reaction conditions, in entry 6 of Table 1, for the acetyl-protected **5b** (entry 7) resulted in no detectable consumption of the donor, and some decomposition of Umemoto's reagent was detected over the 24 hour period of irradiation. The sulfur atom in **5b** is much more resistant to oxidation[12] and has attenuated nucleophilicity relative to the sulfur in the analogous tetrabenzyl series.[1d,e] Reaction of a sulfur atom with an activated intermediate may be inhibited with **5b**. We also screened **5c–e** (entries 8–10) using the reaction conditions of entry 6, and observed no consumption of these donors. Species like **5c** are highly reactive toward activation by thiophilic electrophiles[,1d,e] while the electron-rich nature of the arylthio moiety of **5e** makes it particularly amenable to oxidation by SET.[12]

We investigated the substrate scope of the reaction (Table 2) by using the reaction conditions specified in entry 6 of Table 1. Glycosylations of 1-octanol, cyclohexanol, and (−)-menthol with **5a** proved to be high-yielding (Table 2, entries 1–3). As with previous glycosylations, mixtures of anomers were obtained. Further investigations with glucose- and galactose-derived acceptors (entries 4 and 5) demonstrated that more-difficult

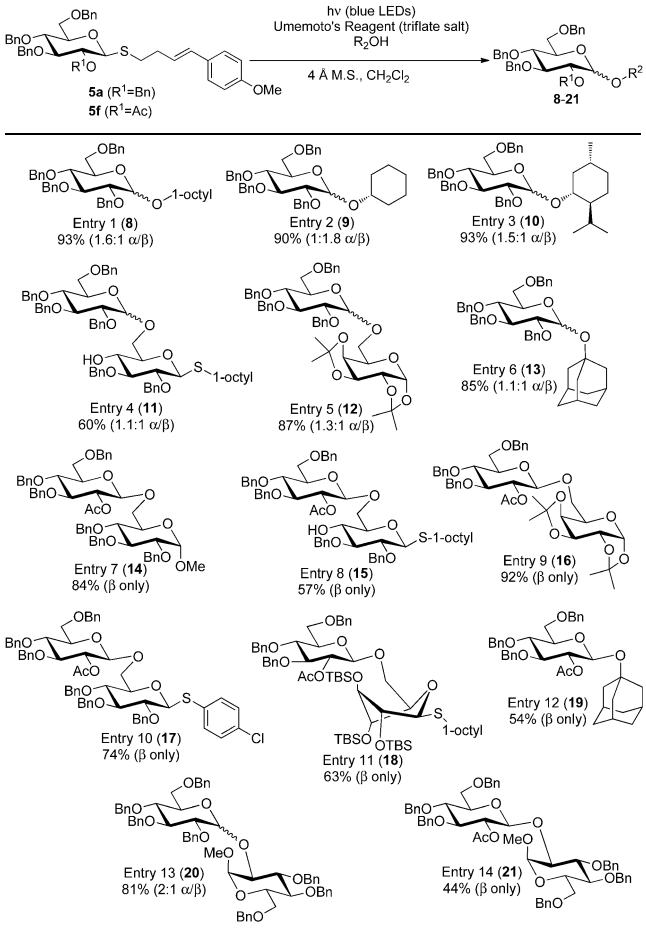
Table 1: Initial screening and optimization.



Entry	Donor	Yield [%][a]	α/β
1	**5a**	55	1.4:1
2[b]	**5a**	0	n.a.
3[c]	**5a**	0	n.a.
4[d]	**5a**	50	1.3:1
5[d,e]	**5a**	76	1.1:1
6[d,e,f]	**5a**	75	1.6:1
7[d,e,f]	**5b**	0	n.a.
8[d,e,f]	**5c**	0	n.a.
9[d,e,f]	**5d**	0	n.a.
10[d,e,f]	**5e**	0	n.a.

Unless otherwise stated, 0.15 mmol of the donor **5**, 1 mol% $Ru(bpy)_3(BArF)_2$, 1.07 equiv Umemoto's reagent, 1.2 equiv DTBMP, 3 equiv of the acceptor **6**, and 300 mg 4 Å M.S. in 2 mL CH_2Cl_2 were irradiated for 24 h with blue LEDs. Reactions maintained a temperature of about 30 °C. [a] Yields of isolated products. [b] No irradiation. [c] No Umemoto's reagent. [d] No $Ru(bpy)_3(BArF)_2$. [e] Used 0.5 equiv of **6**, 150 mg 4 Å M.S. in 1 mL CH_2Cl_2. [f] DTBMP omitted. M.S. = molecular sieves.

Table 2: Scope of reaction.



Unless otherwise stated, 0.15 mmol of the donor **5**, 1.07 equiv Umemoto's reagent, 0.5 equiv of the acceptor, and 150 mg 4 Å M.S. in 1 mL CH_2Cl_2 were irradiated for 24 h with blue LEDs. TBS = *tert*-butyldimethylsilyl.

linkages can be forged readily, while the results of entry 6 demonstrate the compatibility of this method with a tertiary acceptor, namely 1-adamantanol. The results of entry 4 demonstrate the orthogonality of this method toward alkyl-thioglycosides.

Stereoselectivity was low with benzyl groups present at the 2-position of **5a**. By contrast, the donor **5f**, bearing an acetate at the 2-position provided complete β-selectivity (Table 2, entries 7–12) by neighboring group participation. Finally, we demonstrate that challenging linkages involving the glycosylation of a secondary carbohydrate acceptor are possible with this method (entries 13 and 14). The silyl-protected substrate (entry 11) deserves further comment. The so-called superarmed thioglycoside alcohol precursor is approximately 20 times as reactive as the analogous tetra-benzyl-protected thioglucoside toward conventional activation methods.[13,14] The fact that our reaction conditions provided substantial yields of the glycosidic product without any detected oligomerization of the silylated acceptor is remarkable and attests to the orthogonality of this method. Such an effect may prove to be very useful in the one-pot or multistep synthesis of oligosaccharides.

With the establishment of substrate scope, we wished to investigate the mechanism of this transformation. Proton NMR spectra of crude *O*-glycosylation mixtures demonstrated that substantial quantities of an unidentified product were present. This compound was separated (as a single diastereomer) from dibenzothiophene with some difficulty using silica gel chromatography. Based on a combination of 1D and 2D NMR spectroscopy, comparison of coupling constants to those of reported tetrahydrothiophenes,[15] as well as mass spectrometry and polarimetry, we assigned the structure (±)-**22** to this species (Figure 1). This finding lends credence to a glycosylation process which bears some mechanistic resemblance to that in Scheme 1.

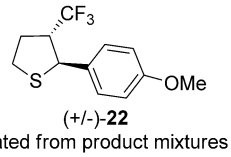


Figure 1. Tetrahydrothiophene by-product

We found that running the reaction under the reaction conditions depicted in entry 6 of Table 1, in the presence of 15 mol% TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) resulted in a yield (72%) which was nearly as high as that obtained in its absence (see the Supporting Information). Finally, experiments conducted in an NMR tube, which was intermittently irradiated and kept in the dark (see the Supporting Information), demonstrated that this reaction requires continuous irradiation to proceed. These pieces of evidence weigh against a radical-chain process. However, the aforementioned on/off light experiment does not rule out short-chain processes[16] and the lack of any TEMPO effect does not prove that radical intermediates are not present.[17] Indeed, EPR spectroscopy detected the formation of a trifluoromethyl radical (by spin-trapping; see the Supporting Information) in an irradiated reaction mixture.

We also observed that CH_2Cl_2 and CH_3CN solutions of Umemoto's reagent and the donors **5a/b** turned yellow upon mixing (see the Supporting Information for photograph) whereas similar solutions of **5c–e** remained colorless. Further, dissolution of Umemoto's reagent and *p*-methoxystyrene in CH_3CN resulted in formation of the familiar yellow color, thus suggesting that the *p*-methoxystyrene moiety is necessary and sufficient for color change to occur. Recent work[9] has demonstrated that EDA complexes, marked by the appearance of color upon dissolution of the electron donor and electron acceptor, can be activated with visible light in synthetic transformations. UV-vis spectrophotometry of mixtures of 26.6 mM Umemoto's reagent and varying concentrations of **5a** in CH_3CN (Figure 2) demonstrated the appearance of a new absorbance tailing into the visible region and with an extinction at the 455 nm wavelength associated with blue LEDs. We attribute this phenomenon to the generation of an EDA complex by interaction of **5a/b** and Umemoto's reagent. Importantly, Umemoto's reagent is

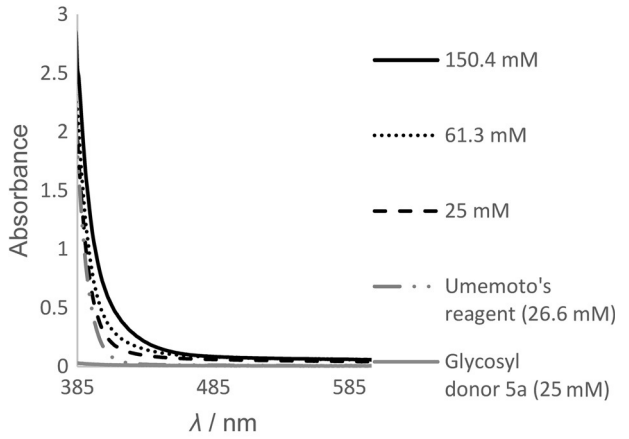
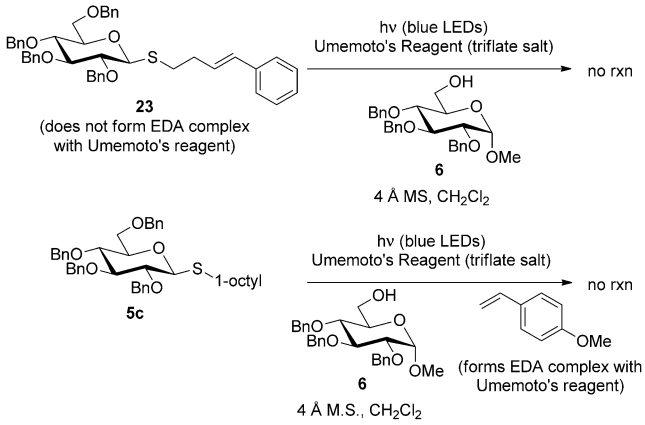


Figure 2. Evidence for an EDA complex (varying concentrations of **5a** in the presence of 26.6 mM of Umemoto's reagent in CH_3CN)

known to form EDA complexes with species other than styrenes.[18]

We observed that the glycosyl donor **23** (Scheme 2) did not generate a yellow color upon dissolution with Umemoto's reagent. Further, spectrophotometry showed little or no evidence for the EDA complex (see the Supporting Information). To study the relevance of the EDA complex in the



Scheme 2. Role of an EDA complex in *O*-glycosylation.

glycosylation reaction, we subjected **23** to glycosylation conditions and determined that it was unreactive. Further, we irradiated **5c** in the presence of 1 equivalent of *p*-methoxystyrene under glycosylation conditions. This combination also proved to be unreactive. These results demonstrate that the EDA complex is necessary for reactivity and that the activation of thioglycoside is intramolecular.

To gain further insight into the possibility of an EDA complex, we conducted computational investigations on a model system consisting of the complex of styrene and 4-methoxystyrene with the *S*-trifluoromethyldibenzothiophenium cation of Umemoto's Reagent (Figure 3). Our electronic structure calculations (using DFT) on the ground-state complex for each system revealed that the charge transfer for certain low-lying isomers of the methoxystyrene/Umemoto's

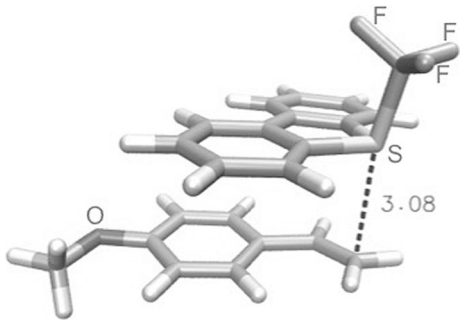
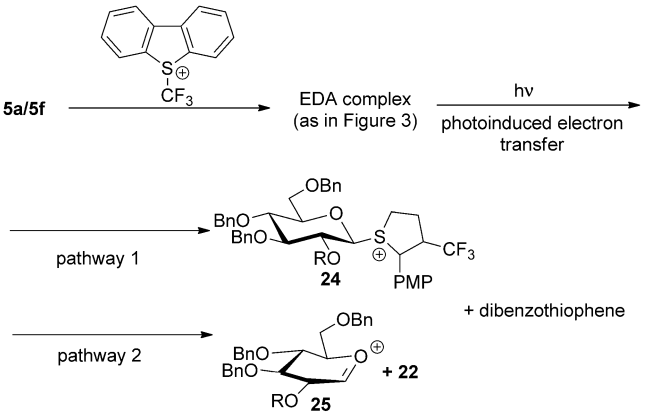


Figure 3. Structure of the EDA complex having the highest charge transfer between Umemoto's reagent and 4-methoxystyrene as determined with DFT calculations.

reagent complex was around 50% higher than that of the styrene complex. The interplanar distance in these complexes is around 3 Å, which is consistent with literature values for EDA complexes.[19] The TD-DFT[20] calculations of the UV-VIS spectra showed that, unlike the styrene case, the methoxystyrene complexes have a strong transition around $\lambda = 500$ nm. Although the results are not quantitative, these calculations do show that there is a transition in the visible region of the spectrum which is consistent with the experimental results. The computational approach and the results are discussed in greater detail in the Supporting Information section.

We propose a preliminary mechanism based on our computational and experimental investigations (Scheme 3). The formation of an EDA complex of **5a** (or **5f**) by π–π stacking of the *p*-methoxystyrene moiety with the *S*-trifluoromethyldibenzothiophenium cation is a prerequisite to absorption of a photon. After absorption of a photon, a subsequent series of events involving the addition of trifluoromethyl and the intramolecular addition of the sulfur atom of **5a**/**5f** across the styrene double bond will result in the direct formation of either **24** (pathway 1) or **25** + **22** (pathway 2). During the conversion of the EDA complex into **24**/**25**, *S*-trifluoromethyldibenzothiophenium may undergo reduction by photoinduced electron transfer from the thioglycoside sulfur atom to generate the trifluoromethyl radical and dibenzothiophene. This SET process would be expected to be more facile



Scheme 3. Preliminary mechanistic proposal.

with the electron-rich tetrabenzyl-protected thioglycosides than with the tetraacetyl-protected analogues, thus potentially explaining the difference in reactivity seen with **5a** and **5b**. Rapid attack of the trifluoromethyl radical onto the styrene double bond before escape from the solvent cage may explain the lack of any negative effect of TEMPO, while occasional escape from the solvent cage would result in spin-trapping observed with EPR. Regardless, the formation of either **24** or **25** are reasonable conduits toward *O*-glycosylation.

In conclusion, we have demonstrated that visible-light irradiation of 4-*p*-methoxyphenyl-3-butenylthioglucoside donors in the presence of Umemoto's reagent serves as a mild approach to *O*-glycosylation. Photocatalysts are not required for activation. Alkyl- and arylthioglycosides are inert to these reaction conditions, and evidence suggests that an intervening EDA complex is necessary for reactivity. Yields with primary, secondary, and tertiary alcohol acceptors range from moderate to high, and complete β-selectivity can be attained through neighboring-group participation. Future efforts will be directed toward attaining α-selectivity, one-pot and iterative synthesis of oligosaccharides, and experimental and computational studies to further elucidate the mechanism of this visible-light-promoted *O*-glycosylation.

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