

Tellurium-Mediated Cycloaromatization of Acyclic Enediynes under Mild Conditions

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The cycloaromatization of easily prepared enediynes¹ is becoming a reliable tool for the formation of fused aromatic systems. Recent explorations of the synthetic aspect of enediyne chemistry have led to the preparation of aromatic rings fused to saturated ring systems,² of linear acenes and *peri*-condensed naphthalenes,³ as well as of highly substituted poly(paraphenylene)s⁴ and cross-linked polymers.⁵ The discovery of technologically promising electronic properties in fused aromatic compounds⁶ underscores the importance of new synthetic routes to such systems.

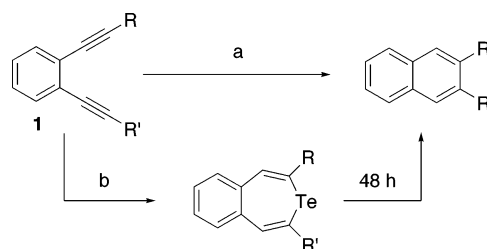
A significant drawback to the cycloaromatization reactions of the synthetically useful acyclic enediynes is the high temperature required for the reaction (typically in excess of 180 °C) combined with the expense of the volatile hydrogen atom source required for the reaction. Both of these factors severely reduce material throughput, limiting the utility of the reaction. Inducing cycloaromatization of enediynes under milder conditions has been an active area of research for the past decade. Photochemical Bergman reactions, for example, have been reported to occur at room temperature, but typically require specific substitution of the alkynes (i.e., **1**, R = R' = alkyl or aryl), and the high dilution conditions required to avoid intermolecular reactions further limit synthetic applicability.⁷ The promotion of cycloaromatization with organometallic species has proved to be a somewhat more versatile strategy, with the most common approach involving the functionalization of the ends of the enediyne with ligands or metal chelators.⁸ Other approaches involve addition of vinylidene carbene to a monosubstituted enediyne⁹ and rate acceleration by aryl complexation of Cp*Ru to a cyclic enediyne.¹⁰ These systems all undergo cycloaromatization at lower temperatures in the presence of metal ions, the drawback being the requirement of specific functional groups on the alkynes.

In 1991, Tsuchiya and co-workers explored the synthesis of benzotellurepines by the hydrotelluration of an enediyne.¹¹ While the expected benzotellurepine was indeed formed in good yield, the authors noted that the major decomposition product of this species was naphthalene – in essence, the cycloaromatization product! In light of the rich chemistry that has since been developed around the reaction of tellurium and tellurides with alkynes,¹² we decided to investigate hydrotelluration as a milder alternative to thermal cycloaromatization of acyclic enediynes.

The conditions reported for the reaction shown in Scheme 1 (path b, R = R' = H) involved the addition of sodium telluride to a biphasic (benzene/water) mixture of the arenediyne, hydrazine, and phase-transfer catalyst. Our investigations of this reaction had the goals of finding an alternative to expensive and air-sensitive sodium telluride,¹³ optimizing conditions for efficient conversion to the cycloaromatized product, and exploring the range of functionality tolerated by the reaction.

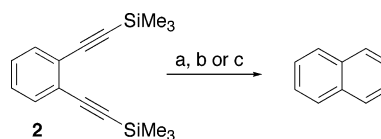
Sodium telluride is conveniently generated from tellurium powder and sodium borohydride in water. To stabilize the aqueous borohydride solution, sodium hydroxide was added to this aqueous

Scheme 1^a



^a Reaction conditions: (a) 180 °C, benzene, 1,4-cyclohexadiene, sealed vessel. (b) Na₂Te, hydrazine, benzene/water, PTC, 60–70%.

Scheme 2^a



^a Reaction conditions: (a) benzene, 10% aqueous NaOH, hydrazine, 1.1 equiv of Te⁰, 2 equiv of NaBH₄, Aliquat 464, 40 °C, ultrasound 8 h, 73%. (b) benzene, 10% aqueous NaOH, hydrazine, 0.1 equiv of Te⁰, 2 equiv of NaBH₄, Aliquat 464, 40 °C, ultrasound, 24 h, 69%. (c) benzene, 40% aqueous NaOH, 1 equiv of Te⁰, 3 equiv of NaBH₄, Aliquat 464, 200 W tungsten lamp, 60 °C, 6 days, 65%.

layer. Fortunately, this added base also performs desilylation of enediynes such as **2**, allowing direct conversion of the more stable silylated enediynes to the cycloaromatized product. Performing this reaction in an ultrasonic bath leads to efficient mixing of the aqueous and organic layers and dramatically accelerates the rate of the reaction (most likely at the Te extrusion step).¹⁴

As shown in Scheme 2a, desilylation/cycloaromatization of the simple silylated arenediyne occurs in >70% yield at 40 °C, using stoichiometric Te⁰. This reaction is scalable, with only a slight decrease in yield (68%) on a 5-g scale of **2**. In principle, regeneration of the telluride during the course of the reaction could be exploited to make the reaction catalytic in Te⁰. Indeed, the reaction proceeds in nearly the same yield when only 10 mol % of tellurium is used, with the only difference being an increase in reaction time (Scheme 2b). In practice, the low cost, low toxicity, and ease with which the tellurium byproducts can be removed make the faster stoichiometric reaction more synthetically useful.

It has been speculated that the addition of telluride to alkynes proceeds by a radical-anion-chain mechanism, with the hydrazine acting as an electron donor.¹⁵ Recent reports of carbottelluration of alkynes under illumination¹⁶ led us to suspect that the hydrazine could be eliminated if the reaction were carried out photochemically. Thus, the conditions shown in Scheme 2c were used to produce naphthalene in 65% yield. While the ability to carry out the reaction in the absence of reactive hydrazine is advantageous, the significant increase in reaction time again makes the thermal conditions more generally useful.

Table 1. Tellurium-Mediated Cycloaromatization Reactions of Substituted Arenediynes

		R = n-Hexyl	65% ^a
		R = OEt	62% ^a
			30% ^{a,b}
			25% ^a
			66% ^{a, c}
		R' = n-Hexyl	6 products ^a
		R' = H	60% ^a

^a Benzene, 10% aqueous NaOH, N₂H₄, 1.1 equiv of Te^o, 2 equiv of NaBH₄, Aliquat 464, 40 °C, sonication, 8 h. All yields isolated. ^b Thermal cycloaromatization gave fluoranthene in <2% yield. ^c An additional 13% of dehalogenated material (2-*tert*-butylnaphthalene) was also formed.

Arenediynes substituted on the aromatic ring also underwent tellurium-mediated cycloaromatization under these conditions (Table 1) in generally good yield. Remarkably, even enediynes that underwent thermal cycloaromatization in very poor yield, such as diethynyl acenaphthylene **4**,¹⁷ formed the expected cycloaromatization product in reasonable yield under these conditions. The extremely reducing conditions required for reaction do limit the functional groups tolerated. These conditions can be used to an advantage, as 4-nitroarene diyne **5** underwent desilylation, cycloaromatization, and reduction to 2-aminonaphthalene in a single step.

Although an explicit hydrogen atom source is not required for the tellurium-mediated reaction, the hydrotelluration of alkynes is still a radical process.¹⁸ While intermolecular polymerization reactions were not observed even in reactions run at relatively high (>0.4 M) concentrations, intramolecular radical reactions were observed in the case of the tellurium-catalyzed cycloaromatization of alkylated **7** (R' = hexyl). Just as with the attempted thermal cycloaromatization of this compound,¹⁹ the tellurium-mediated cycloaromatization led to an inseparable mixture of compounds, all containing the anthracene chromophore, that appeared to be products of hydrogen atom abstraction or cyclization with the adjacent alkyl groups. In contrast, the unsubstituted derivative (**7**, R' = H) produced anthracene in good yield. The radical nature of the hydrotelluration intermediate, just as with the diradical intermediate of the Bergman reaction, limits the groups that can be placed ortho to the alkynes.

Nonaromatic enediynes typically undergo hydrotelluration with the opposite regiochemistry of the corresponding aryl species²⁰ and did not undergo cycloaromatization under these conditions, instead forming intractable mixtures of oligomeric species. Aromatic

enediynes further substituted on the alkyne were also not amenable to cycloaromatization under these conditions.²¹ Disubstituted derivatives (**1**, R = R' = alkyl or aryl) were completely unreactive, while monosubstituted derivatives (**1**, R = H, R' = alkyl) underwent hydrotelluration of the terminal alkyne (in poor yield), but no further reaction occurred even at elevated (>100 °C) temperature.²²

In conclusion, we have demonstrated a rapid, mild, and scalable tellurium-mediated cycloaromatization reaction. The reaction conditions tolerate the typical functionality required for solubilization of organic electronic materials based on polycyclic aromatic compounds and allow the large-scale preparation of technologically important fused aromatic systems in generally good yield.

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Supporting Information Available: Experimental procedures and characterization data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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