

Note

A modified synthesis of tellurophene using NaBH_4 to generate sodium telluride

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ABSTRACT

A modified synthesis of tellurophene by reaction of diacetylene with sodium telluride is described. The primary modification involves the convenient in situ generation of sodium telluride by reduction of tellurium metal with NaBH_4 in water.

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1. Introduction

Tellurophene derivatives have received increased attention in recent years, most notably as potential components of advanced materials [1] and as substrates for the laser-induced chemical vapor deposition (CVD) of tellurium metal films [2]. There is also interest in tellurophenes as potential medicinal agents, particularly as selenium heterocycles have been shown to possess unique biological activities [3]. The development of synthetic methodology for tellurophenes has likewise received increased attention. For example, Zeni and coworkers have recently described the transition metal-catalyzed coupling of 2-bromotellurophenes with either acetylenes [4] or thiols [5]. Others have also developed new chemistry in this area, such as that involving bi- and ter-tellurophenes [1] and 3-iodotellurophenes [6]. Despite this recent work, however, tellurophene chemistry remains a relatively underdeveloped field, with a major hurdle being the lack of availability of the parent heterocycle, as noted recently by several authors [1b,4,5,7].

For our own work, we were in need of multi-gram quantities of tellurophene. The original synthesis [8] of this compound involves the reaction of sodium telluride (Na_2Te) with diacetylene, an unstable gas [9]. Neither of these two starting materials are commercially available. A modification involving the in situ generation of diacetylene from commercially available 1,4-dichloro-2-butyne has subsequently been described [9]. Unfortunately, this procedure is still limited by the need to prepare and isolate the unstable telluride before hand, such as by reduction of tellurium metal with

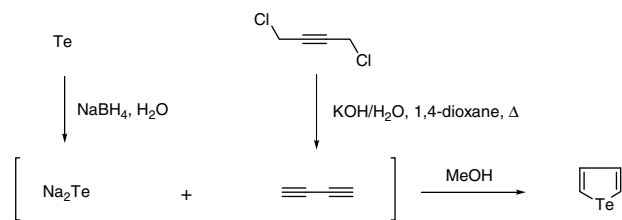
sodium in liquid ammonia [9]. A procedure involving the in situ generation of the telluride by reduction of tellurium with sodium formaldehyde sulfoxylate (Rongalite) has also been described [10], but it utilizes the expensive bis(trimethylsilyl)-1,3-butadiyne as a substitute for diacetylene [11]. This particular procedure has also been difficult for us to reproduce, with reduction of the tellurium not proceeding in suitable fashion in our hands. We thus set out to develop a modified synthesis, with the most desirable being one that not only utilizes in situ generated sodium telluride, but also the less expensive 1,4-dichloro-2-butyne as a source of diacetylene. In this note, we describe our favorable results.

2. Results and discussion

Having had difficulty in generating sodium telluride in situ by reduction of tellurium with sodium formaldehyde sulfoxylate, we looked for other possible reducing agents. Upon review of the literature, the most appealing to us was NaBH_4 , particularly as it can be used in an aqueous solvent system [12]. We thus explored this approach.

In contrast to the sulfoxylate, the reaction of NaBH_4 with tellurium metal in water gave, in our hands, clear evidence of telluride formation (exothermic reaction, formation of characteristic violet color) (Scheme 1). After just 20 min, telluride formation was deemed complete and the diacetylene was then introduced into the reaction mixture by heating 1,4-dichloro-2-butyne (1.5 equiv.) with KOH in a separate flask connected by a gas line. Methanol was also added at this point to the telluride suspension to help solubilize the diacetylene. Importantly, the entire system was kept under nitrogen throughout the process, as sodium telluride is very oxygen sensitive.

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Scheme 1. Synthesis of tellurophene by in situ generation of Na_2Te and diacetylene.

After stirring for 2 h, the reaction mixture was immediately extracted and the residue distilled under vacuum to give tellurophene as a pale red liquid in 32–48% yield. As a comparison, the comparable literature procedure which uses pre-formed sodium telluride, as well as ~5 molar equivalents of 1,4-dichloro-2-butyne (compared to our 1.5 equiv.), reportedly gives an average yield of 48% [9]. As an alternative to distillation, we could isolate the insoluble 1,1-dibromotellurophene adduct [9] as a red solid in 45% yield by addition of methanolic Br_2 to the extract. Reduction of this adduct back to tellurophene using bisulfite, followed by extraction and distillation, gave tellurophene in 37% overall yield as a yellow liquid, which was identical otherwise with the pale red samples prepared by direct distillation.

3. Conclusion

In conclusion, a modified synthesis of tellurophene involving the in situ generation of sodium telluride by reduction of tellurium with NaBH_4 in water is presented. With this procedure, tellurophene can be conveniently prepared in 32–48% yield using just 1.5 molar equivalents of 1,4-dichloro-2-butyne as a commercial source of diacetylene, and without the need to first prepare, and isolate, the unstable sodium telluride.

4. Experimental

Complete details for the synthesis of tellurophene by this method are given below:

To a 500 mL 3-neck round bottom flask (flask A) equipped with gas inlet, condenser and addition funnel was added Te powder (200 mesh, Aldrich, 9.53 g, 75 mmol) and NaBH_4 (11.35 g, 300 mmol). A separate 250 mL 3-neck round bottom flask (flask B) was loaded with potassium hydroxide (18.93 g, 337.5 mmol) in water (100 mL). An addition funnel loaded with 1,4-dichloro-2-butyne (Aldrich, 13.73 g, 112.5 mmol) dissolved in 1,4-dioxane (15 mL) was placed in flask B. Gas tubing was run from the top of the condenser on flask B to a glass pipet connected to a side-arm of flask A (the pipet is ultimately submerged into the contents of flask A). An addition funnel was loaded with nitrogen purged MeOH (150 mL) and placed on flask A. At this point, deionized water (150 mL) was added in one portion to flask A and the entire system was charged with nitrogen (nitrogen flow should be minimal in order to later avoid driving the diacetylene out of the system) and stirring begun. After 5–10 min, there was a noticeable discharge of hydrogen gas occurring and the water began to boil (an ice bath was intermittently used to control the reaction). After 20 min, the tellurium was fully reduced giving a light pink or violet suspension. At this point, flask A was cooled in an ice bath and MeOH (150 mL) was added. At the same time, flask B was brought to vigorous reflux after addition of the 1,4-dichloro-2-butyne. After another 20 min, the ice bath was removed from flask A and the reaction left alone for 2 h as the diacetylene was being introduced

from flask B. After the 2 h, flask B was removed from the heat and flask A was exposed to air. The resulting black suspension in flask A was filtered over Celite and extracted with pentane after addition of brine. The extracts were combined and concentrated on a rotary evaporator at atmospheric pressure. The remaining dark liquid was distilled at reduced pressure (house vacuum) using a short Vigreux column (8 cm) to give 4.28–6.42 g (32–48% yield, $n = 4$) of tellurophene as a light red liquid boiling at 120 °C (lit. bp [9] 91–92 °C at 100 mmHg). The product was pure by GC. ^1H NMR (400 MHz, CDCl_3 , TMS reference at 0.0 ppm): δ 7.83 (dd, $J = 5.6, 2.4$ Hz), 8.95 (dd, $J = 5.6, 2.8$ Hz). ^{13}C NMR (100.6 MHz, CDCl_3 , solvent reference at 77.5 ppm): δ 126.7 (s), 138.3 (s). MS (EI, m/z , %): 182 (C_4H_4 $^{130}\text{Te}^+$, 100), 130 ($^{130}\text{Te}^+$, 74), 51 (45), 40 (23). These data are consistent with those previously published [9,10].

As an alternative to direct distillation, the extract could be treated with a 30% solution of bromine in methanol to give 1,1-dibromotellurophene as a highly insoluble red solid (11.4 g, 45%) (in this case, diethyl ether was used as an extraction solvent in place of pentane). This adduct (m.p. 125 °C dec; lit mp [9] 125 °C dec) was immediately reduced back to tellurophene by stirring for 20 min in a solution of 26 g NaHSO_3 and 16 g K_2CO_3 dissolved in water (200 mL). This mixture was then extracted with ether, dried (Na_2SO_4) and distilled under reduced pressure as above to give 5.0 g (37% overall yield) of a yellow liquid boiling at 120 °C.

The tellurophene was stored in a freezer (0 °C) and showed no visual degradation over the course of several months. The 1,1-dibromotellurophene was stored in a closed amber vial at room temperature and decomposed to a black metallic solid over the course of several months.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.022.

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