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Preliminary communication

A convenient synthesis of tellurophene

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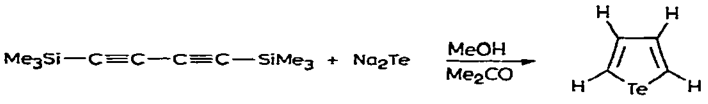
It is likely that the recent, definitive studies of Fringuelli and Taticchi[1,2] on the chemistry and aromatic character of the tellurophene ring system will stimulate considerable research on this heteroaromatic ring[★]. At present the parent tellurophene (I) must be of paramount interest. This molecule was first described by Mack[4] in 1966 but experimental details were sparce. A complete experimental procedure for this synthesis of tellurophene has recently been published by Fringuelli and Taticchi[1]. These authors prepared sodium telluride from sodium and tellurium in liquid ammonia. This was then allowed to react with 1,3-butadiyne which was generated externally from 1,4-dichloro-2-butyne in a painstaking procedure requiring relatively complex apparatus and large volumes of deoxygenated solvents to afford tellurophene in 47% yield. A predictable reluctance to work with these reagents, especially the dangerous butadiyne, and the complexity of the procedure could serve as a major deterrent to those wishing to study the parent tellurophene.

We report here a convenient preparation of tellurophene from reagents which are readily available, with common laboratory apparatus and which avoids the troublesome and potentially dangerous external generation of butadiyne. Our method simply involves addition of an acetone solution of the stable, readily prepared[5] bis(trimethylsilyl)-1,3-butadiyne (II) to a solution of Na_2Te in methanol to provide, upon work-up, a 37% isolated yield of pure tellurophene.



(II) (I)

Although the yield is somewhat lower than that reported by the Italian workers, this is more than offset by the convenience of the procedure. Indeed, 37% should probably be considered a minimum yield as (1) these reactions have been performed only on

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[★] For a review of work prior to refs. 1 and 2 see ref. 3.

relatively small scales (ca. 0.02 mol maximum), (2) a product distillation step was included which is probably not necessary, (3) deoxygenated solvents were not used and (4) Na_2Te of uncertain purity was employed. Although in the reaction reported here Na_2Te prepared from elemental sodium and tellurium was employed, we have used commercial Na_2Te with success in the synthesis of tellurophenes.

It should be noted that while this reaction would formally give 2,5-bis(trimethylsilyl)tellurophene, the methanolic Na_2Te solution is undoubtedly of sufficient basic character to cleave[6] the trimethylsilyl groups from II to provide *in situ* generation of 1,3-butadiyne.

EXPERIMENTAL

NMR spectra were recorded on a Varian HA-100 spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded on a Beckman IR 12 spectrometer as liquid films. Bis(trimethylsilyl)-1,3-butadiyne was prepared by the method of Ballard and Gilman[5] and further purified by recrystallization from acetone. Sodium telluride was prepared by the reaction of molten sodium with tellurium metal. Sodium telluride is commercially available from Rocky Mountain Research Corp., Denver, Colorado 80204.

Tellurophene (I)

Sodium telluride (4.53 g, 26.0 mmol), previously weighed in a nitrogen atmosphere and transported in a capped vial, was added under a stream of argon to 66 ml of absolute methanol (freshly opened bottle) in a 250 ml flask equipped with an addition funnel, argon inlet tube and magnetic stirrer. After dissolution of the Na_2Te, a solution containing 4.12 g (21.2 mmol) bis(trimethylsilyl)-1,3-butadiyne in 50 ml acetone (freshly opened bottle) was added dropwise over 1h at room temperature. After stirring an additional 3h the solution was exposed to air to oxidize any excess Na_2Te and then filtered to remove the black precipitate. The pale yellow filtrate was concentrated to ca. 25 ml by distillation at atmospheric pressure[★] and the remainder taken up in 60 ml ether. Dropwise addition of bromine to the methanol distillate precipitated 1.37 g tellurophene dibromide resulting from codistillation. A stirred suspension of the dibromide in ether (15 ml) was treated with sodium bisulfite (2.46 g) until all of the dibromide was reduced[4]. The ether layer was separated and combined with the etheral solution of the distillation residue. This combined solution was washed with water (3 × 10 ml), dried ($MgSO_4$) and concentrated by distillation at atmospheric pressure. Distillation of the residue at 100 mm afforded 2.085 g of volatile material (there is some evidence that this distillation step can be omitted) which was chromatographed on basic alumina (Baker, 45 g, 3 × 10 cm) with 130 ml pentane. Evaporation of the pentane left 1.412 g (37%) of pure (VPC) tellurophene.

NMR in $DCCl_3$: $\delta 7.81$ (2H, m), $\delta 8.93$ (2H, m). IR (m or s) 3090, 1435, 1318, 1249, 1231, 1082, 985, 799, 675 cm^{-1}.

[★] Concentration of methanolic solutions of tellurophene under reduced pressure results in an appreciable loss of product (ref. 2).

ACKNOWLEDGEMENT

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