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o-Quinonoid Heterocycles: Benzo[*c*]tellurophene.

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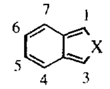
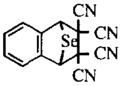
Abstract: The first synthesis of the *o*-quinonoid heterocycle benzo[*c*]tellurophene (**5**) has been achieved. Compound **5**, prepared in two steps from the known 1,3-dihydrobenzo[*c*]tellurophene diiodide (**6**), was characterized spectroscopically, and by Diels-Alder trapping reactions. Copyright © 1996 Elsevier Science Ltd

The highly reactive o-quinonoid heterocycles benzo[c]furan (**1**) and benzo[c]thiophene (**2**) have been investigated from the synthetic as well as theoretical points of view.[1,2] The latter has attracted particular attention in recent years as the precursor of the low band-gap conducting polymer poly(benzo[*c*]thiophene).[3] The unstable selenium analog **3** was first prepared by us *via* a base-catalyzed selenoxide dehydration, and trapped as its TCNE adduct **4**.[4] In contrast, neither the tellurium analog **5**, nor any derivative thereof, has been hitherto reported. We now report the first synthesis of the elusive benzo[*c*]tellurophene (**5**). The readily prepared, highly insoluble 1,3-dihydrobenzo[*c*]tellurophene diiodide (**6**)[5] was converted to the soluble bistrifluoroacetate **7** by reaction with silver trifluoroacetate in benzene.[6] Reaction of the bistrifluoroacetate **7** in refluxing benzene with triethylamine cleanly generated benzo[*c*]tellurophene (**5**) in ~ 80% yield along with its reduction product **8** (~ 20%). Heterocycle **5** was stable in benzene solution under an inert atmosphere for prolonged periods, but its solutions in chloroform or DMSO darkened within days. It was also unstable towards acid, and could not be chromatographed on silica or alumina.



1 X = O **3** X = Se
2 X = S **5** X = Te



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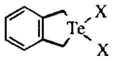
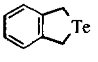


6 X = I
7 X = OCOCH$_3$



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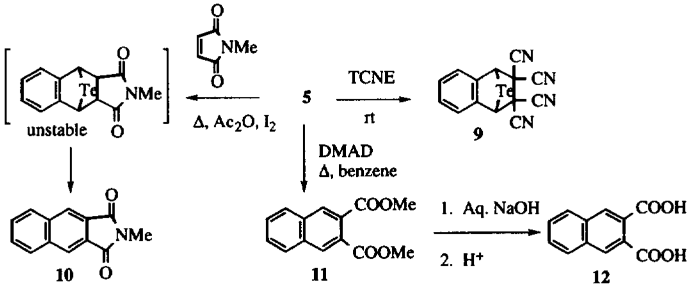
The nmr spectrum of **5**, deduced by a process of elimination of the signals for the known **8**, showed the H_1, H_3 signals as a downfield singlet and the H_4 - H_7 resonances as a pair of doublets, the positions of which depended on the solvent. For example, in $CDCl_3$ and DMSO(d_6) the downfield H_1,H_3 singlet was at 9.34 δ, H_4, H7 resonances (dd) at δ 7.32 (J=6.99, 3.20 Hz) and H_5, H_6 (dd) at δ 6.72 (J=6.72, 2.92 Hz). In deuteriobenzene these resonances shifted to higher fields (8.80, 7.10, and 6.64). As expected, the UV absorption spectrum of **5** shows bathochromic shifts in comparison with the selenium analog **3**. The maxima occur at λ 339, 366 and 387 nm in benzene solution.

Benzo[*c*]tellurophene (**5**) reacted in the cold readily with TCNE to furnish the orange crystalline adduct **9**.[7] In contrast, its reactions with N-methylmaleimide and dimethyl acetylenedicarboxylate at room temperature were sluggish.



Reaction of the bistrifluoroacetate **7** with N-methylmaleimide in acetic anhydride in the presence of iodine led to the isolation of imide **10** in 10% yield, identical (nmr, ir, mp) with an authentic sample. Refluxing a benzene solution of freshly prepared **5** with DMAD led to the isolation of diester **11** in 25% yield, (nmr δ 8.0, s, 2H; dd at 7.9 and 7.6, 2H each, 3.95, s, 6H) which was hydrolyzed to give the known dicarboxylic acid **12**, identical with a commercial sample.

Benzo[*c*]tellurophene (**5**) is transformed into a shiny black solid upon standing in the free state under nitrogen at ambient temperature. The nature of this polymeric material is currently under investigation.

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6. **7**, mp. dec > 160 °C; nmr spectrum ($CDCl_3$), s, 4H, δ 7.30; s, 4H, δ 4.76.
7. **9**, mp. dec 134 °C; nmr spectrum (DMSO D_6) dd, 2H, δ 7.30 (J=8.4 Hz, 3 Hz); dd, 2H, δ 7.08 (J=8.6 Hz, 3 Hz); s, 2H, δ 5.30.

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