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Facile Reaction of *Te*-Aryl Benzenecarbotelluroates, ArCOTeAr′, with Methyl Iodide and Halogens

Harkesh B. SINGH* and Narasimhan SUDHA
Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400076, India
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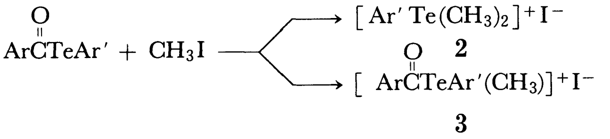
Synopsis. Reaction of *Te*-aryl benzenecarbotelluroates of the type ArCOTeAr′ (Ar=phenyl *p*-tolyl, *p*-bromophenyl; Ar′=phenyl, *p*-methoxyphenyl) with methyl iodide was found to give symmetrical telluronium salts, $[\mathrm{Ar'Te(CH_3)_2}]^+\mathrm{I}^-$ in good yields. The reactivity of one of these benzene carbotelluroates towards halogens was also examined.

Although diaryl and dialkyl tellurides are known to react with methyl iodide to form the corresponding telluronium salts (Scheme 1),[1] it has been newly found that reaction of *Te*-aryl benzenecarbotelluroates with methyl iodide results in cleavage of the Te–CO bond.

$$\mathrm{R_2Te + CH_3I \rightarrow [R_2(CH_3)Te]^+I^-}$$

Scheme 1.

When benzenecarbotelluroates (**1a—d**) were treated with excess of methyl at room temperature for 48 h, colorless $[\mathrm{Ar'Te(CH_3)_2}]^+\mathrm{I}^-$ (**2a—b**) were formed in yields of 70—90% based on the used tellurides **1**, together with trace amounts of as yet uncharacterized dark-violet compounds (Scheme 2) which contain carbonyl function. In no reaction was obtained the expected product **3**.



3

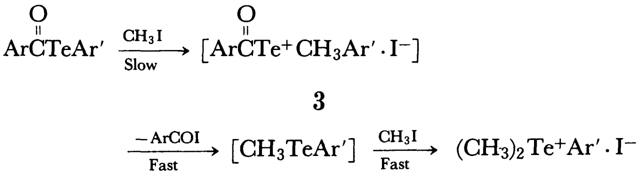
1a: Ar′=$\mathrm{C_6H_5}$, Ar=$\mathrm{C_6H_5}$
1b: Ar′=$\mathrm{C_6H_5}$, Ar=*p*-$\mathrm{BrC_6H_4}$
1c: Ar′=$\mathrm{C_6H_5}$, Ar=*p*-$\mathrm{CH_3C_6H_4}$
1d: Ar′=*p*-$\mathrm{CH_3OC_6H_4}$, Ar=*p*-$\mathrm{CH_3C_6H_4}$

2a: Ar′=$\mathrm{C_6H_5}$
2b: Ar′=*p*-$\mathrm{CH_3OC_6H_4}$

Scheme 2.

Whereas the halogenolysis reactions of similar compounds, tellurophthalide and tellurophthalic anhydride have been reported earlier,[2] to the best of our knowledge no reaction of benzenecarbotelluroates with methyl iodide has been previously described.

The scheme which most reasonably accounts for the results can be written as follows:



$$\mathrm{Ar\overset{O}{\overset{\|}{C}}TeAr'} \xrightarrow[\text{Slow}]{\mathrm{CH_3I}} \underset{\mathbf{3}}{[\mathrm{Ar\overset{O}{\overset{\|}{C}}Te^+CH_3Ar'\cdot I^-}]}$$

$$\xrightarrow[\text{Fast}]{-\mathrm{ArCOI}} [\mathrm{CH_3TeAr'}] \xrightarrow[\text{Fast}]{\mathrm{CH_3I}} \underset{\mathbf{2}}{\mathrm{(CH_3)_2Te^+Ar'\cdot I^-}}$$

In order to learn more about the behavior of the Te–CO bond, we have investigated the halogenolysis reactions of **1d**. It was found that the benzenecarbotelluroate reacted with excess of $\mathrm{SO_2Cl_2}$, $\mathrm{Br_2}$, or $\mathrm{I_2}$ at room temperature to afford the corresponding $\mathrm{Ar'TeX_3}$ (X=Cl, Br, I) via cleavage of the Te–CO bond.

Experimental

Materials and Instruments. The *Te*-aryl benzenecarbotelluroates were prepared by the reaction of a benzoyl chloride with NaTeAr′.[3] All compounds had melting points and ν_{CO}'s in good agreement with those reported in the literature. IR spectra (4000—600 cm^{-1}) were obtained in KBr discs with Perkin Elmer 681. ^{1}H NMR (100 MHz) were obtained with a JEOL FX 100 instrument. Elemental analysis was by the Analytical Services Section, Regional Sophisticated Instrumentation Centre, Lucknow.

Reaction of $\mathrm{C_6H_5TeCOC_6H_5}$ with $\mathrm{CH_3I}$. To the benzenecarbotelluroate (0.25 g, 0.8 mmol) was added methyl iodide (2—3 ml) in a 50 ml flask and then capped. The resulting solution was allowed to stand for 48 h at ambient temperature during which time yellowish crystals separated out and the color of the solution turned dark-red. After 48 h absolute ether (10 ml) was added to the reaction mixture and allowed to stand for additional 12 h. The crystals were filtered, washed with ether, recrystallized from ethanol/water (1 : 1) to yield white crystals of $[\mathrm{C_6H_5Te(CH_3)_2}]^+\mathrm{I}^-$; yield 0.2 g (70% based on **1a** used), mp 168 °C.[4] Calcd (Found): C, 26.5 (25.9%); H, 3.06 (3.51%). ^{1}H NMR (DMSO-d_6) δ=2.38 (s, 6H), 7.5—7.9 (m, 5H). The red mother liquor was evaporated to dryness and the residue was washed with petroleum ether (40—60 °C) to give a dark violet solid of indefinite composition. IR (KBr) 1685 cm^{-1} (ν_{CO}). Reactions of $\mathrm{C_6H_5TeCOC_6H_4Br}$-*p* and $\mathrm{C_6H_5TeCOC_6H_4CH_3}$-*p* with $\mathrm{CH_3I}$ also gave $[\mathrm{C_6H_5Te(CH_3)_2}]^+\mathrm{I}^-$ in excellent yields (ca. 90%) and trace quantities of the brownish red solids. Reaction of *p*-$\mathrm{CH_3OC_6H_4TeCOC_6H_4CH_3}$-*p* with $\mathrm{CH_3I}$ yielded [*p*-$\mathrm{CH_3OC_6H_4Te(CH_3)_2}]^+\mathrm{I}^-$ in excellent yield (ca. 86%), mp 172 °C (lit,[5] 170—172 °C). Calcd (Found) : C, 27.5 (26.9%); H, 3.34 (3.57%). ^{1}H NMR (DMSO-d_6) δ=2.3 (s, 6H), 3.8 (s, 3H), 7.0—7.8 (m, 4H). A brownish red solid of indefinite composition was also obtained.

Halogenolysis Reactions. In a typical reaction, to a solution of *p*-$\mathrm{CH_3OC_6H_4TeCOC_6H_4}$-*p* (0.4 g, 1.13 mmol) in chloroform (25 mL) was added dropwise iodine (0.28 g, 1.13 mmol) dissolved in chloroform at room temperature during 30 min. *p*-$\mathrm{CH_3OC_6H_4TeI_3}$ is continuously precipitated as a dark violet solid, mp 130 °C (d), yield 0.35 g (91%) (based on **1d** used). Analogous reactions of $\mathrm{Br_2}$ and $\mathrm{SO_2Cl_2}$ with **1d** afforded *p*-$\mathrm{CH_3OC_6H_4TeBr_3}$ and *p*-$\mathrm{CH_3OC_6H_4TeCl_3}$ which were characterized by comparison with authentic samples (mp, IR, ^{1}H NMR).[1]

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