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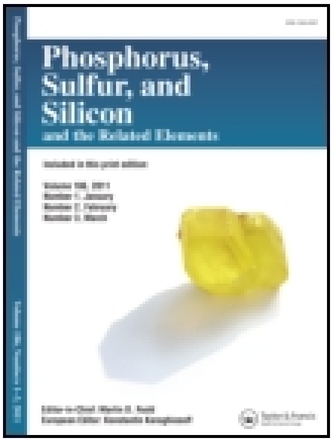

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

PHASE TRANSFER CATALYSIS IN SYNTHESIS OF ORGANYLTHIO (ORGANYLTELLURO) ACETYLENES

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Published online: 24 Sep 2006.

To cite this article: Alexander V. Martynov , Anna N. Mirskova & Georges Le Guillanton (1998) PHASE TRANSFER CATALYSIS IN SYNTHESIS OF ORGANYLTHIO (ORGANYLTELLURO) ACETYLENES, Phosphorus, Sulfur, and Silicon and the Related Elements, 133:1, 245-250, DOI: 10.1080/10426509808032470

To link to this article: http://dx.doi.org/10.1080/10426509808032470

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Phosphorus, Sulfur and Silicon, Vol. 133, pp. 245-250
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PHASE TRANSFER CATALYSIS IN SYNTHESIS OF ORGANYLTHIO(ORGANYLTELLURO) ACETYLENES

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(Received 28 October, 1997)

Phase transfer reaction of diorganyl ditellurides with organyl-2,2-dichlorovinyl sulfides, using as phase transfer catalysts benzyltriethylammonium chloride or 18-crown-6 ether, was used as a new general method to prepare organylthio(organyltelluro)acetylenes R-S-C≡C-Te-R′. The organyltellurolate anion formed in the presence of NaOH is the reaction intermediate.

Keywords: Organylthio(organyltelluro)acetylenes; diorganyl ditellurides; PTC; organyl-2–2-dichlorovinyl sulfides

INTRODUCTION

Organylthio(organyltelluro)acetylenes R-S-C≡C-Te-R′ **1** were known only as alkyl derivatives (R = Me, Pr, R′ = Me)[1], obtained by insertion of elemental tellurium into the C-Na bond of acetylenide R-S-C≡CNa and subsequent nucleophilic substitution of the halogen atom in alkyl halide with the resulting tellurolate anion (Scheme 1).

But it is quite clear that it is impossible to obtain ethynyl aryl tellurides (**1**, R′ = Ar) by this process.

In order to develop a general method to prepare acetylenes **1** we studied the phase transfer reaction of organyl-2,2-dichlorovinyl sulfides **2** with ditellurides **3**.

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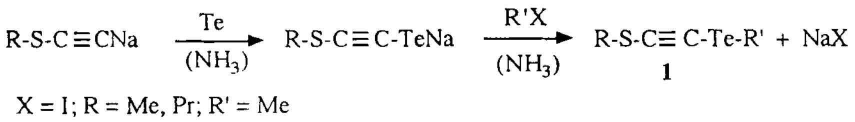
* Correspondence and reprints.



$$\text{R-S-C}\equiv\text{CNa} \xrightarrow[(\text{NH}_3)]{\text{Te}} \text{R-S-C}\equiv\text{C-TeNa} \xrightarrow[(\text{NH}_3)]{\text{R'X}} \underset{\mathbf{1}}{\text{R-S-C}\equiv\text{C-Te-R'}} + \text{NaX}$$

X = I; R = Me, Pr; R' = Me

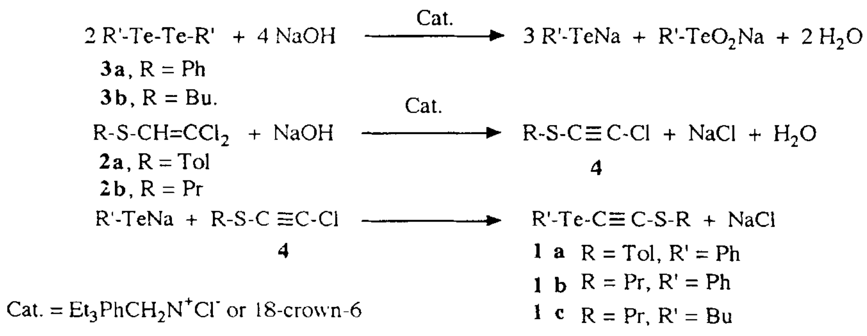
SCHEME 1

Earlier we found out that the similar reactions of sulfides **2** with diselenides could lead both to organylthio(organylseleno)acetylenes or to 1,2-bis(organylseleno)- 1-organylthio-2-chloroethylenes[2], depending on the reaction conditions. Formation of these compounds was due to generation of selenolate anions[3] and organylthiochloroacetylenes[4] in the reaction mixture. Since the same alkaline cleavage of chalcogen-chalcogen bond is characteristic also for ditellurides[5], we tried to use this method to synthesize acetylenes **1**.

RESULTS AND DISCUSSION

We have found that the use of the aforementioned method of primary generation of chalcogenolate anion in the reaction mixture and its consequent reaction with sulfides **2** , is workable in the case of diorganyl ditellurides **3** and makes possible to obtain acetylenes **1**, including ones with a aryltelluro group.

If we refer to published works for diselenides[3,4], formation of these compounds can be explained by generation of tellurolate anions R-Te⁻ and organylthiochloroacetylenes R-S-C≡C-Cl **4** in the reaction mixture (Scheme 2).



$$2\,\text{R'-Te-Te-R'} + 4\,\text{NaOH} \xrightarrow{\text{Cat.}} 3\,\text{R'-TeNa} + \text{R'-TeO}_2\text{Na} + 2\,\text{H}_2\text{O}$$

3a, R = Ph

3b, R = Bu.

$$\text{R-S-CH=CCl}_2 + \text{NaOH} \xrightarrow{\text{Cat.}} \underset{\mathbf{4}}{\text{R-S-C}\equiv\text{C-Cl}} + \text{NaCl} + \text{H}_2\text{O}$$

2a, R = Tol

2b, R = Pr

$$\text{R'-TeNa} + \underset{\mathbf{4}}{\text{R-S-C}\equiv\text{C-Cl}} \longrightarrow \text{R'-Te-C}\equiv\text{C-S-R} + \text{NaCl}$$

1 a R = Tol, R' = Ph

1 b R = Pr, R' = Ph

1 c R = Pr, R' = Bu

Cat. = $\text{Et}_3\text{PhCH}_2\text{N}^+\text{Cl}^-$ or 18-crown-6

SCHEME 2

Another pathway for formation of acetylenes **1** by direct reaction of organyltellurolate anions with sulfides **2** followed by dehydrochlorination of chloroethylene **5**, is not excluded (Scheme 3). Isolation and characterization of 1-propylthio-2-butyltelluro-2-chloroethylene **5a** (33% yield) as a main by-product in the reaction of propyl-2,2-dichlorovinyl sulfide **2b** with dibutyl ditelluride **3b**, speaks in favor of the latter reaction path, though both ways are most likely to occur simultaneously.

$$\text{R'-TeNa} + \text{R-S-CH=CCl}_2 \longrightarrow \text{(Z),(E)-R-S-CH=CCl-Te-R'} + \text{NaCl}$$

5 R = Pr, R' = Bu.

$$\underset{\mathbf{5}}{\text{(Z),(E)-R-S-CH=CCl-Te-R'}} + \text{NaOH} \xrightarrow{\text{Cat.}} \underset{\mathbf{1}}{\text{R-S-C}\equiv\text{C-Te-R'}} + \text{NaCl} + \text{H}_2\text{O}$$

SCHEME 3

Acetylenes **1** were obtained in pure form by column chromatography (silicagel, eluent cyclohexane:CH_2Cl_2 / 95:5). Separation by distillation in vacuo was inefficient and leads to fractions which contain acetylenes with 85–89% purity, according to GLC data. Besides acetylenes **1**, some by-products were identified by Chromatomass-spectrometry, GLC and HPLC data: starting material **2** and **3**, diphenyl telluride in the case of reaction with ditelluride **3a** and bis(organylthio)acetylenes R-S-C≡C-S-R **6** (8% yield). This latter compound isolated and characterized, can arise from the hitherto unknown PTC reaction of organylthiochloroacetylenes **4** with organylthiolate anion coming from disulfides always formed as admixtures during the synthesis of **2**[8] (scheme 4).

$$2\,\text{R-S-S-R} + 4\,\text{NaOH} \longrightarrow 3\,\text{R-SNa} + \text{R-SO}_2\text{Na} + 2\,\text{H}_2\text{O}$$

$$\underset{\mathbf{4}}{\text{R-S-C}\equiv\text{CCl}} + \text{R-SNa} \longrightarrow \text{R-S-C}\equiv\text{C-S-R} + \text{NaCl}$$

6a R = Tol
6b R = Pr

SCHEME 4

Is theses reactions diethyl ether was utilized as solvent, because it was proved to be efficient in the PTC reaction with diselenides[2]. But since ditellurides are very unstable in the oxygen-containing solvents being oxidized to insoluble telluroxides by dioxygen[7], we used also benzene in order to exclude this side reaction. But even in this solvent we failed to obtain tolylthio(butyltelluro)acetylene **1c** in the reaction of tolyl-2,2-dichlorovinyl sulfide **2a** with dibutyl ditelluride **3a**.

Only parent sulfide **2a** and tolylthiochloroacetylene Tol-S-C≡CCl **4** resulting from it, were separated from the black tar obtained here.

EXPERIMENTAL

Organyl-2,2-dichlorovinyl sulfides **2** were prepared by free radical thiylation of trichloroethylene[8].

IR spectra were recorded on a Biorad FTS 155 spectrometer (film or KBr pellet), ^1H NMR spectra on a JEOL PMX 60 SI spectrometer at 60 Mhz (solvent $CDCl_3$, TMS as internal standard, δ in ppm). HPLC analyses were carried out on a chromatograph Spectra-Physics SP 8700 with SP8440 XR UV/VIS detector and computing integrator SP4200, HPLC column SPHERI-5 ODS. GLC analyses were carried out on a chromatograph Chrom 5, glass column 2.5 m, chromaton NAW (0.200–0.250 mm) with 5% silicon SE 30, inerton AW-HMDS (0.200–0.250 mm) with 5% silicon XE-60. Chromatomass-spectra were obtained on LKB 2091 spectrometer at electron energy 70 eV, ion source temperature 250°C, capillar column, silicon SE 30.

PREPARATION OF ORGANYLTHIO(PHENYLTELLURO)ACETYLENES

General procedure

10 mM of diorganyl ditelluride **3** were stirred for 6.5 h under nitrogen atmosphere with a mixture of 60 ml of 50% NaOH and 40 ml of benzene in the presence of 2–4 mM of benzyltriethylammonium chloride (BTEAC) (with benzene) or 2 mM of 18-crown-6 ether (with ether). Then 15 mM of organyl-2,2-dichlorovinyl sulfide **2** in 10 ml of benzene were introduced during 20 min. Into this mixture another 2–4 mM of BTEAC (but no 18-crown-6) were added and it was stirred for 3–7 h in the case of propyl-2,2-dichlorovinyl sulfide **2b**, or 21 h in the case of phenyl-2,2-dichlorovinyl sulfide **2a** and then was diluted with 100 ml of H_2O and extracted with diethyl ether or dichloromethane. Extracts were washed with diluted solution of hydrochloric acid and dried over $CaCl_2$. After removal of the solvent, the residue was distilled in vacuo (except for acetylene **1a**) and the product mixture was separated by column chromatography on silicagel (cyclohexane:CH_2Cl_2 / 95:5) to obtain the pure acetylenic compound.

TOLYLTHIO(PHENYLTELLURO)ACETYLENE, Tol-S-C≡C-Te-Ph, 1a

Yield 67% ; m.p. 48–49°C (EtOH) (100% purity according to HPLC); ν_{max} 3045, 2910, 2856, 2056s, 1571s, 1490, 1472, 1433, 1180, 1117, 1010, 1014s, 996, 840, 805vs, 732vs, 688s, 652, 502s, 480s, 446s cm^{-1} ; δ_H 2.33s (3H, CH_3), 7.30m (7H), 7.70m (2H) (C_6H_5, C_6H_4, A_2X_3+ A_2B_2). Found %: C 50.60, 50.69; H 3.28, 3.41; S 9.01; Te 36.01. $C_{15}H_{12}STe$. Calculated %: C 51.19; H 3.44; S 9.11, Te 36.26.

From the same mixture bis(tolylthio)acetylene Tol-S-C≡C-S-Tol **6a** was obtained. Yield 8.5%; m.p. 99–99.5°C (EtOH); lit.[6]: m.p. 98–99°C. Found %: C 71.01; H 5.15; S 23.89. $C_{16}H_{14}S_2$. Calculated %: C 71.07; H 5.22; S 23.71.

PROPYLTHIO(PHENYLTELLURO)ACETYLENE, Pr-S-C≡C-Te-Ph, 1b

Yield: 44%; b.p. 145–160°C (2 torr); ν_{max} 3052s, 2962s, 2929s, 2871, 2055s, 1573s, 1473, 1457, 1434s, 1418, 1377, 1327, 1291s, 1263, 1235s, 1156, 1093, 1061s, 1017s, 997s, 898s, 838s, 781s, 726vs, 686s, 651, 615 cm^{-1}; δ_H 1.03t (3H, CH_3), 1.77m (2H, CH_2), 2.73t (2H, CH_2), 7.70m(2H) and 7.30m (3H) (C_6H_5). MS: polyisotopic molecular ion $[M]^+$ at m/z(relative intensity calculated/found) 308(5/6), 306(100/100), 305(12/15), 304(90.8/94), 302(55/ 59), 301(21.2/21.7), 300(13.4/ 15) and fragment ions $[PhTe]^+$ at m/z (^{130}Te) 207, $[M\text{-}Te]^+$at m/z(^{130}Te) 176, [Ph-C≡C-SH]$^+$. at m/z 134, $[Ph]^+$ at m/z77 and $[Pr]^+$ at m/z 43. Found %: C 43.46, 43.66; H 3.90, 3.92; S 9.90, 9.56; Te 40.18, 40.24. $C_{11}H_{12}STe$. Calculated %: C 43.48; H 3.98; S 10.55; Te 41.99.

Also were detected diphenyl telluride PhTePh, giving polyisotopic molecular ion $[M]^+$ at m/z(relative intensity calculated/found) 285(13.5/12.6), 284(100/100), 283(12.5/16), 282(92/84.5), 280(56.7/60), 279(22/25.6), 278(13.7/16.6) and diphenyl ditelluride **3a** with $[M]^+$ at 414(50.7/42.5), 412 (93/83.4), 410(100/100), 408(66.5/66.5), 407(26/29.7), bis(propylthio)acetylene **6b** with molecular ion $[M]^+$ at m/z 174 and fragment ions [PrSC≡CSH]$^{+\cdot}$ at m/z 132, [HSC≡CSH]$^{+\cdot}$ at m/z 90 and $[Pr]^+$ at m/z 43.

By use of 18-crown-6 with Et_2O as solvent, the yield was the same.

PROPYLTHIO(BUTYLTELLURO)ACETYLENE, Pr-S-C≡C-Te-Bu, 1c

18-Crown-6 was used as catalyst. The main fraction obtained by distillation contains **1c** and some amounts of the ditelluride **3b**. Treatment of this mixture with methanol for 12 h leads to oxidation of BuTeTeBu to form methanol insoluble oxides. After stripping of methanol from the filtered solution pure acetylene **1c** was obtained.

Yield 31%; b.p. 100–102°C(1 torr); n^{20}_D 1.5840 (100% purity according to HPLC); ν_{max}2961vs, 2929s, 2872, 2733, 2057s, 1601, 1461s, 1418, 1378, 1340, 1292s, 1245, 1237, 1182, 1164, 1087, 1059, 966, 888, 831, 778, 704, 585vs, 503 cm^{-1} ; δ_H 0.93t (6H, CH_3), 1.63m (6H, CH_2), 2.70dt (4H, CH_2). Found %: C 37.57; H 5.53; S 10.95, 9.56; Te 44.02,. $C_9H_{16}STe$. Calculated %: C 38.08; H 5.68; S 11.29; Te 44.95.

1-Propylthio-2-butyltelluro-2-chloroethylene **5** Pr-S-CH=CCl-Te-Bu was also isolated and characterized. Yield 33%; b.p. 55–60°C (2 torr); n^{20}_D 1.5218; ν_{max} 2962, 2928, 2873, 1739s, 1566, 1458, 1422, 1377s, 1294, 1217s, 1160, 910s, 842, 820, 791, 732, 635, 507vs, 484s, 452s, 437, 425 cm^{-1} ; δ_H 1.03t (6H, CH_3) 1.67m (6H, CH_2, C_2H_4), 2.63t, 2.80t (4H, CH_2), 6.40s (1H, =CH); MS: polyisotopic molecular ion $[M]^+$, m/z(relative intensity calculated/found) 322(100/100), 324(83/94), 318(45/84), 317(16/63), fragment ions $[M\text{-}Cl]^+$and $[M\text{-}HCl]^+$, m/z 286, 284, 282.

Acknowledgements

This study was supported partly by the grant 166868D of Ministère des Affaires Etrangères (France).

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