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A new approach to the synthesis of symmetrical bis(organylchalcogeno)acetylenes: Scope and limitations

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Summary — A new general method to prepare bis(organylchalcogeno)acetylenes R-Y-C≡C-Y-R (Y = S, Se, Te) by dehydrochlorination of the corresponding 1,2-bis(organylchalcogeno)chloroethylenes R-Y-CH=CCl-Y-R with *tert*-BuOK/*tert*-BuOH and/or KOH/DMSO is developed. Dechlorination of 1,2-bis(organylchalcogeno)-1,2-dichloroethylenes R-Y-CCl=CCl-Y-R (Y = S, Se, Te) with BuLi in ether or THF is effective only for sulfur derivatives. With Y = Se and alkyl substituents, substitution of the chlorine atom by a butyl group takes place giving rise to 5,6-bis(alkylseleno)dec-5-ene [Bu-C(SeR)=C(SeR)-Bu]. With aryl substituents, an attack of the ArSe-group by the Bu-radical is observed leading to an aryl butyl selenide. In the case of the tellurium compound Ph-Te-CCl=CCl-Te-Ph, there is a competition between dechlorination to give Ph-Te-C≡C-Te-Ph, and substitution to produce the phenyl butyl telluride.

bis(organylchalcogeno)acetylene / 1,2-bis(organylchalcogeno)chloroethylene / 1,2-bis(organylchalcogeno)-1,2-dichloroethylene / dehydrochlorination / dechlorination / butyllithium

Résumé — Nouvelles voies de synthèse de bis(organylchalcogéno)acétylènes symétriques: possibilités et limitations. Une nouvelle méthode de préparation des bis(organylchalcogéno)acétylènes R-Y-C≡C-Y-R (Y = S, Se, Te) est proposée mettant en jeu la déshydrohalogénation des 1,2-bis(organylchalcogéno)chloroéthylènes R-Y-CH=CCl-Y-R correspondants par *tert*-BuOK/*tert*-BuOH et/ou KOH/DMSO. La déshalogénation des 1,2-bis(organylchalcogéno)-1,2-dichloroéthylènes R-Y-CCl=CCl-Y-R (Y = S, Se, Te) par BuLi dans l'éther ou le THF n'est possible qu'avec les dérivés sulfurés. Lorsque Y = Se et R = alkyl, la substitution de l'atome de chlore par un groupement butyl est observée conduisant au 5,6-bis(alkylséléno)déc-5-ène Bu-C(SeR)=C(SeR)-Bu. Dans le cas des substituants aromatiques, l'attaque du groupe Ar-Se par le radical butyl donne l'aryl butyl séléniure. Deux réactions se déroulent simultanément dans le cas de Ph-Te-CCl=CCl-Te-Ph, la déshalogénation conduisant à Ph-Te-C≡C-Te-Ph et la substitution donnant le phényl butyl tellurure.

bis(organylchalcogéno)acétylène / 1,2-bis(organylchalcogéno)chloroéthylène / 1,2-bis(organylchalcogéno)-1,2-dichloroéthylène / déshydrohalogénation / déshalogénation / butyllithium

Introduction

One of the most interesting types of bis-substituted acetylenes are symmetrical bis(organylchalcogeno)-acetylenes R-Y-C≡C-Y-R [R = Alkyl, Ar, Y = S (**1**), Se (**2**), Te (**3**)] possessing the properties of both unsaturated compounds and chalcogenes. So, bis(alkylthio)acetylenes **1** and bis(methylseleno)acetylenes (**2a**, R = Me) can be polymerized to form poly-[bis(alkylchalcogeno)acetylenes]: $[-C(YR)=C(YR)-]_n$ (Y = S, Se, R = Alkyl), which in turn can be doped with electron acceptors to produce semiconductors [1,2]. Bis(methylthio)acetylene (**1a**, R = Me) gives with bromine 1,2-bis(methylthio)-1,2-dibromoethylene [3] and undergoes cycloaddition reaction with *N*-(methylthio)phthalimide to form spirothietes [4]. Bis(organylthio)acetylenes (**1b**, R = Ph; **1c**, R = Tol; **1d**, R = *tert*-Bu) can be oxidized to bis(arylsulfonyl)acetylenes R-SO_2-C≡C-SO_2-R (R = Ph, Tol, *tert*-Bu) with dimethyldioxirane [5] or *m*-chloroperbenzoic acid [6].

A number of methods to produce these acetylenes **1**–**3** were developed during the last thirty years. Sulfur containing acetylenes R-S-C≡C-S-R **1** were obtained in 35-38% yield by the Wurtz-type reaction of ethynedithiolates NaS-C≡C-SNa with alkyl halides [7,8], in 29-58% yield by thermolysis of bis(alkylthio)ethenes Ph_3P=S-CH-C(SR)$_2$ [9], in 45% yield by treatment of 1,2-bis(methylthio)vinyl diethyl amine Me-S-CH=C(SMe)-NEt_2 with lithium [10], by decomposition of 3,4-bis(alkylthio)cyclobutane-1,2-dione [11], in 50-100% yield by substitution of chlorine in organylthiochloroacetylene R-S-C≡C-Cl with organylthiolate [12,13], in 82% yield by in-

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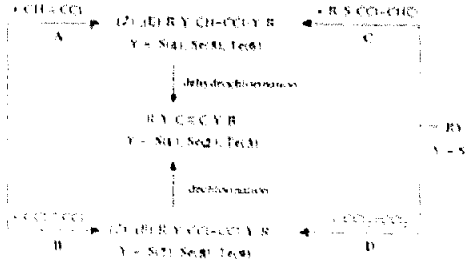
teraction of lithio chloroacetylene LiC≡C–Cl with dialkyl disulfides [14], in 70% yield by reaction of bis(phenyl[perfluoroalkanesulfonyloxy]iodo)-acetylene, PhI⁺–C≡C–I⁺–Ph-2R$_f$SO$_3^-$, with organylthiolate [15,16].

Bis(alkylseleno)acetylenes R–Se–C≡C–Se–R **2** can be produced in 70–80% yield by disproportionation reaction of ethynyl selenide, CH≡C–Se–R, obtained in turn by the aforementioned Wurtz-type reaction of ethyneselenolate, CH≡C–SeNa, with alkyl halides [7], in 57% yield by the aforesaid reaction of 1,2-bis(methylseleno)vinyl diethylamine, Me–Se–CH=C(SeMe)NEt$_2$, with lithium [10], by decomposition of 3,4-bis(alkylseleno)cyclobutane-1,2-dione [11], by dehydrobromination of alkyl 2-bromovinyl selenide R–Se–CH=CHBr with KOH in DMSO that affords along with the expected ethynyl selenide R–Se–C≡CH, bis(alkylseleno) acetylenes **2** in yields up to 100%, depending on the conditions of the reaction [17]. Two methods to obtain bis(arylseleno)acetylenes are known. These include substitution of H in ethynyl selenide, Ph–Se–C≡CH, with phenylselenenyl bromide in the presence of CuI giving bis(phenylseleno)acetylene **2b** in 58% yield [18] and substitution of both H and Me$_3$Si in Me$_3$Si–C≡CH with the PhSe group generated from Ph–Se–Se–Ph in the presence of iodobenzene diacetate PhI(OAc)$_2$, giving acetylene **2b** in 41% yield [19]. But no data on the physical constants of these acetylenes were given in these works.

Bis(alkyltelluro)acetylenes **3** (R = alkyl) were prepared in 60–70% yield by interaction of lithium ethynetellurolate, CH≡C–TeLi, or dilithium ethynediditellurolate, LiTeC≡CTeLi, with alkyl iodides in the presence of ethylenediamine [20] or in 90% yield by interaction of dialkyl ditellurides with acetylene in the presence of methyl iodide in the phase transfer conditions [21]. Bis(aryltelluro)acetylenes **3** (R = aryl) are unknown.

In this work new methods to prepare bis(organylchalcogeno)acetylenes **1**–**3** are proposed using dehydrochlorination of 1,2-bis(organylchalcogeno)chloroethylenes **4**–**6**, or dechlorination of 1,2-bis(organylchalcogeno)-dichloroethylenes **7**–**9** (scheme 1).



Scheme 1

Earlier one of us has developed facile syntheses of 1,2-bis(organylseleno)chloroethylenes R–Se–CH=CCl–Se–R (**5**, R = Alkyl, Ar) [22,23] and 1,2-bis(organylseleno(tellluro)-1,2-dichloroethylenes R–Y–CCl=CCl–Y–R (**8**, Y = Se, R = Alkyl, Ar [22,23]; **9**, Y = Te, R = Ar [24]) by dichalogenation of chloro- or dichloroacetylene with diorganyl dichalcogenides R–Y–Y–R (Y = Se, Te) (scheme 1, A and B). Analogous 1,2-bis(organylthio)chloroethylenes R–S–CCl=CH–S–R **4** can easily be obtained by substitution of Cl with an RS group in the 1,2-dichlorovinyl sulfides [25–27] (scheme 1, C). (*E*)-1,2-Bis(organylthio)-1,2-dichloroethylenes R–S–CCl=CCl–S–R (**7**, R = Alkyl, Ar) arise in the reaction of organylthiolates with tetrachloroethylene [28–30] (scheme 1, D).

Results and discussion

Preparation of the parent compounds

Parent 1,2-bis(organylseleno)chloroethenes R–Se–CH=CCl–Se–R (**5a**: R = Me, **5b**: R = Ph) were prepared by the aforementioned diselenation of chloroacetylenes [22,23]. A similar method was used to obtain unknown 1,2-bis(phenyltelluro)chloroethylene Ph–Te–CH=CCl–Te–Ph **6** in an almost quantitative yield (scheme 1, A). Identification of chloroethylene **6** was realized by mass spectrum and by ^{1}H NMR spectrum (table 1) where among the signals of the benzene protons in a range of δ, ppm 7.00–7.50m (6H) and 7.50–8.07m (5H) we identified the singlet signal of a vinylic proton at δ 7.67 ppm. The infrared spectrum of the obtained compound was identical to that of the known 1,2-bis(phenylseleno)-chloroethylene Ph–Se–CH=CCl–Se–Ph **5b** [2] (table 1).

1,2-Bis(phenylthio)chloroethylene **4a** (R = Ph) was produced as by-product (36% yield) in a free radical thiylation of trichloroethylene with benzenethiol (scheme 3). We should point out that earlier one of us showed that this reaction led exclusively to the synthesis of organyl-2,2-dichlorovinyl sulfides **10** [31] (scheme 2).

Formation, practically under the same experimental conditions, of large amounts of the unexpected 1,2-bis(organylthio)chloroethylene **4** was probably due to the use of pyrex glassware instead of the quartz and molybdenum ones used in a previous work [31]. As a result under UV-irradiation (high-pressure mercury lamp Q 81 with irradiation range 248–577 nm) in a pyrex glassware, the short-wave part of this irradiation was cut off. On the contrary, under chemical initiation, pyrex glassware appeared transparent for the ultraviolet of direct sunlight. In both cases this seems to have led to enhanced oxidation of benzenethiols to disulfides. We had shown that thiylation with diaryl disulfides differed from that with pure thiols [31].

Based on the results obtained in this work, it could be assumed that under the reaction conditions used, this reaction does not stop at this stage but proceeds further on as a free radical substitution of a chlorine atom in isomeric dichlorovinyl sulfides **10** and **11** to produce chloroethylene **4** according to scheme 3.

1,2-Bis(organylchalcogeno)chloroethylenes were obtained as mixtures of *cis*-*trans* isomers where the *trans* isomer is predominant. 1,2-Bis(organylseleno(tellluro)]-1,2-dichloroethylenes R–Y–CCl=CCl–Y–R (**8**, Y = Se; **9**, Y = Te) were prepared according to a method previously described [22–24] by the reaction of diorganyl diselenides RSe–SeR (R = Me, Ph) and ditelluride R–Te–Te–R (R = Ph) with dichloroacetylene (scheme 1, B). The formation of these compounds as (*E*)-isomers

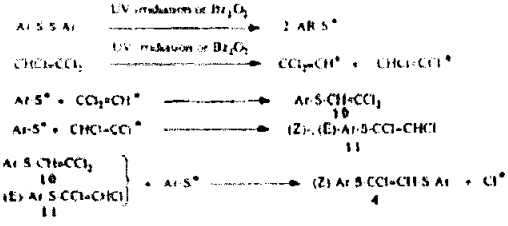
Table I. Physicochemical constants, IR and ^{1}H NMR spectra of 1,2-bis(organylchalcogeno)-chloro- and dichloroethylenes R–Y–CX=CCl–Y–R (Y = S, Se, Te; X = H, Cl).

Compound	*Bp, °C (p, torr) and n_D^{20} or mp, °C*	*IR, ν, cm^{-1}*	*^{1}H NMR, δ, ppm (from Me_4Si)*
PhSCH=CClSPh **4a**	158–184 (2) 1.6688	3 059, 1 947w, 1 581, 1 542, 1 476, 1 439, 1 210, 1 156, 1 088, 1 024, 1 000, 898s, 736s, 685s, 616, 519	7.43 m (5H), 7.17 s (5H), 0.97 s (1H)
MeSeCH=CClSeMe[a] **5a**	62–65 (0.3) 1.6461	3 074, 3 011, 2 929, 2 819, 1 942, 1 422, 1 272, 1 190, 909, 840, 782, 717, 688, 585	6.93 s (1H, =CH), 2.33 s (3H, CH_3), 2.23 s (3H, CH_3)
PhSeCH=CClSePh[b] **5b**	175–180 (0.7) 1.6622	3 071s, 3 058, 3 000, 2 958, 2 928, 2 860, 1 948, 1 875, 1 800, 1 726s, 1 578s, 1 539, 1 476s, 1 439, 1 381, 1 275s, 1 180, 1 125s, 1 071s, 1 022, 1 000, 909, 847s, 789, 736s, 689s, 670, 591, 482	7.83–7.50 m (5H), 7.50–7.20 m (6H)
PhTeCH=CClTePh[c] **6**		3 065, 3 051, 2 990, 1 949, 1 874, 1 806, 1 573, 1 510, 1 473, 1 434, 1 326, 1 300, 1 573, 1 510, 1 473, 1 573, 1 510, 1 473, 1 180, 1 157, 1 063, 1 018, 998, 909, 843, 800, 731s, 690s, 656	8.07–7.50 m (4H), 7.50–7.00 m (6H), 7.67 s (1H, =CH)
(*E*)-PrSCCl=CClSPr[d] **7a**	94–120 (0.5) 1.5530	2 966s, 2 932, 2 873, 1 515, 1 459s, 1 417, 1 379, 1 338, 1 294s, 1 238s, 1 091, 1 053, 971, 863s, 782, 733s, 641, 585	1.03 t (6H), 1.63 hexet (4H), 2.93 t (4H), $^3J_{HH}$ 7 Hz
(*E*)-TolSCCl=CClSTol[e] **7b**	98–99.5 (EtOH)	2 914, 2 856, 1 901, 1 638, 1 565, 1 488, 1 403, 1 302, 1 208, 1 179, 1 114, 1 043, 1 015, 869, 836, 805s, 737, 629, 506s, 426	2.43 s (3H), 7.27 d, 7.47 d (4H, A_2B_2, $^3J_{HH}$ 8–9 Hz)
(*E*)-MeSeCCl=CClSeMe[f] **8b**	88–90 (0.8) 1.6582	2 931, 2 842, 1 516, 1 421s, 1 273, 909s, 818s, 655, 504	2.43 s
(*E*)-PhSeCCl=CClSePh[g] **8a**	94 (EtOH)	3 049, 1 876, 1 576, 1 473, 1 437, 1 326, 1 300, 1 273, 1 177, 1 063, 1 018, 998, 853, 841, 739s, 684s, 637, 469	7.60 m, 7.17 m
(*E*)-PhTeCCl=CClTePh[h] **9**	150–151 (CH_2Cl_2)	3 043, 1 570, 1 516, 1 469, 1 432, 1 325, 1 301, 1 265, 1 177, 1 063, 1 018, 998, 1018, 853, 841, 739s, 684s, 637, 469	7.33 t, 7.17 q (5H, A_2X_3)

[a] Lit [2] bp 86.5 °C (1 torr), n_D^{20} 1.6472. [b] Lit [2] bp 103–104 °C (2 torr), n_D^{20} 1.6855, NMR ^{1}H, δ, ppm: 7.35–7.47 m, 7.03–7.22 m (C_6H_5), 7.21 s (=CH). [c] Yellow oil, used in dehydrochlorination reaction without further purification. [d] Lit [31] bp 90–92 °C (0.4 torr), n_D^{20} 1.5542. [e] Lit [29,31] mp 101–101.5 °C. [f] Lit [31] bp 85.5–87.5 °C (2 torr), n_D^{20} 1.6570. [g] Lit [31] mp 94–94.5 °C. [h] Lit [32] mp 150–151 °C.

Scheme 2

was confirmed by XRD analysis [32,33]. (*E*)-1,2-bis(organylthio)-1,2-dichloroethylenes **7** were obtained by the known reaction of nucleophilic substitution of chlorine atoms in tetrachloroethylene with thiolate anions [28–30] (scheme 1, D).



Scheme 3

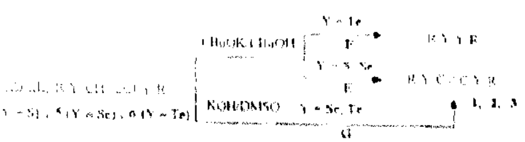
Dehydrochlorination of 1,2-bis(organylchalcogeno)chloroethylenes

To carry out dehydrochlorination of chloroethylenes **4–6**, we tested as dehydrochlorinating agents *tert*-BuOK/*tert*-BuOH and KOH/DMSO which were successfully used in the case of 1-alkylthio-2-organylseleno-2-chloroethylenes R–S–CH=CCl–Se–R′ (R = Et, *i*-Pr, R′ = Ph, Bu) [34]. It was found that with 1,2-bis(phenylthio)chloroethylene **4a**, 1,2-bis(methylseleno)chloroethylene **5a** and 1,2-bis(phenylseleno)-chloroethylene **5b**, both dehydrochlorinating systems were efficient (scheme 4, E). In all cases only bis(organylchalcogeno)acetylenes R–Y–C≡C–Y–R **1, 2** were obtained in good yields (65–95%) and 95–99% purity (table II).

Table II. Conditions of dehydrochlorination of bis(organylchalcogeno)chloroethenes **4**, **5**, **6**.

[illegible]	*Dehydrochlorinating system*	*Reaction temperature (°C)*	*Reaction time (h)*	*Reaction product*	*Yield g (%)*	*Product purity (%) by HPLC*
(*Z*+*E*)-PhSCH=CClSPh **(4a)** 6	2.8 g *tert*-BuOK 150 mL *tert*-BuOH	50	5	PhSC≡CSPh **(1b)**	4.07 (78)	100
(*Z*+*E*)-PhSeCH=CClSePh **(5b)** 3	1 g *tert*-BuOK 100 mL *tert*-BuOH	50	8	PhSeC≡CSePh **(2b)**	2.43 (90)	94
(*Z*+*E*)-MeSeCH=CClSeMe **(5a)** 1.45	0.5 g KOH 12 mL DMSO	20	8	MeSeC≡CSeMe **(2a)**	0.81 (65)	95
(*Z*+*E*)-MeSeCH=CClSeMe **(5a)** 3.26	2 g *tert*-BuOK 15 mL *tert*-BuOH	50	13	MeSeC≡CSeMe **(2a)**	2.64 (95)	100
(*Z*+*E*)-PhTeCH=CClTePh **(6)** 1.2	0.15 g KOH 13 mL DMSO	20	8	PhTeC≡CTePh **(3)**	0.64 (58)	98
(*Z*+*E*)-PhTeCH=CClTePh **(6)** 4	1.2 g *tert*-BuOK 50 mL *tert*-BuOH	50	5	PhTeTePh mp 64–65 °C Identified by IR and mass spectroscopies	2.22 (63)	97

In the case of 1,2-bis(phenyltelluro)chloroethylene **6**, the reaction depended drastically on the dehydrohalogenating agent taken. With *tert*-BuOK/*tert*-BuOH only diphenyl ditelluride was separated (scheme 4, F). With KOH/DMSO, the expected unknown bis(phenyltelluro)acetylene **3** was obtained in 58% yield (scheme 4, G). The formation of this acetylene was indisputably confirmed by [1]H NMR, IR and mass spectra (table III).



Scheme 4

In order to explain different results obtained in this reaction we tested the stability of acetylene **3** in *tert*-BuOK/*tert*-BuOH at 70 °C for 2 h. As found by the TLC in cyclohexane, this acetylene **3** turns first into Ph–Te–Te–Ph which, in these more drastic conditions, ends up as an oxidation product, probably $Ph_2Te_2O_3$ [35]. This is indicated by the high melting point of the formed white crystals (> 300 °C) and by the IR spectrum of this product which is almost identical to that of ditelluride Ph–Te–Te–Ph except for the long-wave region (737–400 cm^{-1}) where strongly widened peaks at 737, 690 and 670 cm^{-1} characteristic for the Te–O bonding [36] were found. It was pointed out that oxidation of ditellurides by dioxygen was strongly catalyzed by alcohols [35] which is in good agreement with the above result. Based on these findings, we can conclude that dehydrochlorination of chloroethylene **6** by *tert*-BuOK/*tert*-BuOH is dictated by the instability of bis(phenyltelluro)acetylene **3** in these basic conditions (scheme 5).

In this regard, reaction of acetylene **3** with *tert*-BuOK resembles cleavage of the ≡C–OR′ bond by organometallics M–R″ (M = Li), terminating in the formation of MOR′ [37]. But it is interesting to note that with ethynyl sulfides and selenides, R–C≡C–Y–R′, the same reagents give saturated chalcogenides and metal acetylenides (scheme 6) [37]. Hence, it follows that the chemical behavior of ethynyl bis-telluride **3** is rather different from that of other chalcogenides, though the reason for this discrepancy is unclear.

Dechlorination of 1,2-bis(organylchalcogeno)-1,2-dichloroethylenes

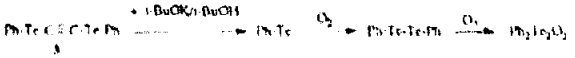
Though it was known that dehalogenation of dihalogenalkenes could be rather easily accomplished with zinc, magnesium and organolithium compounds [25,38–42], in the case of organylchalcogeno-substituted dihalogenoalkenes this reaction was almost unexplored. However, it was known that BuLi causes dehalogenation of polyhalovinyl sulfides such as ethyl 1,2-dichlorovinyl sulfide Et–S–CCl=CHCl [25], butyl 1-fluoro-2,2-dichlorovinyl sulfide Bu–S–CF=CCl_2 [38], trichlorovinyl benzyl sulfide Ph–CH_2–S–CCl=CCl_2 [43] with formation of lithium acetylenide [25,43] or chloroacetylene [38]. A similar reaction of BuLi with 1,1-bis(alkylthio)-2,2-dichloroethylene R–S–C(SR)=CCl_2 was followed by a rearrangement to form bis(organylthio) acetylenes **1**; with 1,1-dichloroalken-2-yl sulfides R–S–C(R′)=CCl_2 a dimeric product R–S–C(R′)=C=C=C(R′)–S–R was obtained [44]. In all cases, dehalogenation was stated to proceed as *trans*-elimination.

Taking into account all stated above, we have tested as dechlorinating agents for *trans*-1,2-bis(organylchalcogeno)-1,2-dichloroethylenes, zinc, magnesium and butyllithium. But neither magnesium in THF, nor zinc in EtOH or acetic anhydride, caused dechlorination of

Table III. Physicochemical constants, IR and ^{1}H NMR spectra of bis(organylchalcogeno)acetylenes R–Y–C≡C–Y–R (Y = S, Se, Te) **1**, **2**, **3**.

Compound, yield %	*bp, °C (p, torr) and n_D^{20} or mp, °C*	*IR, ν, cm^{-1}*	*^{1}H NMR, δ, ppm (from Me$_4$Si)*	*Microanalysis*
Pr–S–C≡C–S–Pr[a] **1e** $C_8H_{14}S_2$ 51	70–71 (1) 1.5435	2 965s, 2 932s, 2 847s, 1 459, 1 418, 1 379, 1 337, 1 292s 1 236s, 1 093, 1 060, 896, 837, 782, 735, 702, 628s, 488	1.00 t (3H), 1.77 hexet (2H), 2.67 t (2H), $^3J_{HH}$ 7 Hz	Found %: C 55.02; H 8.0; S 36.62 Calc %: C 55.12; H 8.10; S 36.78
Ph–S–C≡C–S–Ph **1b** $C_{14}H_{10}S_2$ 78	39–40 (EtOH)	3 050, 1 650, 1 578, 1 477, 1 440, 1 329, 1 303, 1 183, 1 062, 1 060, 1 022, 998, 897, 848, 735, 685, 557	7.70–7.17 m	Found %: C 69.33; H 4.19; S 26.56 Calc %: C 69.38; H 4.16; S 26.46
Tol–S–C≡C–S–Tol[b] **1c** $C_{16}H_{14}S_2$ 98	98–99 (EtOH)	2 916, 2 859, 1 899, 1 639, 1 593, 1 489s, 1 442, 1 399, 1 325, 1 305, 1 208, 1 181, 1 141, 1 117, 1 079, 1 039, 1 013, 839, 805, 654, 619, 585, 527, 481s, 450	7.50 d, 7.27 d (4H, A_2B_2, $^3J_{HH}$ 9–10 Hz), 2.40 s (3H)	Found %: C 71.01; H 5.15; S 23.89 Calc %: C 71.07; H 5.22; S 23.71
Me–Se–C≡C–Se–Me[c] **2a** $C_4H_6Se_2$ 65–90	43 (0.3) 1.6570	2 931s, 2 835, 2 812, 2 174, 2 070, 1 839, 1 488, 1 418, 1 267, 1 146, 915s, 771s, 575, 501, 482	2.33 s	Found %: C 22.72; H 2.82; Se 74.66 Calc %: C 22.66; H 2.85; Se 74.49
Ph–Se–C≡C–Se–Ph **2b** $C_{14}H_{10}Se_2$ 90	54–54.5 (EtOH)	3 050, 1 574s, 1 542, 1 522, 1 509, 1 475s, 1 438s, 1 385, 1 327, 1 302, 1 178, 1 156, 1 097, 1 065, 1 020s, 996, 967, 903, 844, 782, 736s, 689s, 665, 469, 455	7.77–7.53 m (4H), 7.53–7.17 m (6H) (A_2B_3)	Found %: C 49.86; H 2.92; Se 46.66 Calc %: C 50.02; H 3.00; Se 46.88
Ph–Te–C≡C–Te–Ph **3** $C_{14}H_{10}Te_2$ 58	84–86 (EtOH)	3 042, 2 579, 1 567, 1 470, 1 432, 1 299, 1 066, 1 043, 995, 901, 847, 797, 735s, 688, 658s, 458, 419	7.97–7.70 m (4H), 7.53–7.23 m (6H) (A_2B_3)	Found %: C 38.43; H 2.06; Te 58.35 Calc %: C 38.80; H 2.33; Te 58.88

[a] Lit [43]: 69.5 °C (1 torr), n_D^{20} 1.5476. [b] Lit [58]: mp 98–99 °C. [c] Lit [55]: bp 83–84 °C (5 torr), n_D^{20} 1.6589.



Scheme 5

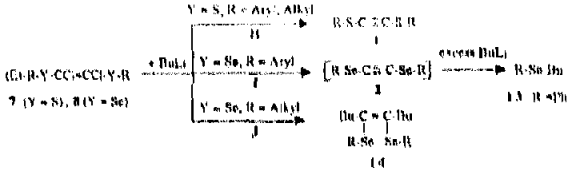
dichloroethylenes **7b**, **8a**, **9**. In the case of butyllithium, at room temperature, the reaction depended on chalcogene and adjoining groups and also on the dichloroethylene/BuLi ratio.

Scheme 6

• *Organylthio compounds*

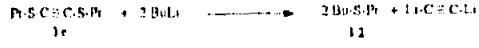
With 1,2-bis(organylthio)-1,2-dichloroethenes R–S–CCl=CCl–S–R (**7a**: R = Pr, **7b**: R = Tol) as the ratio **7**/BuLi equals 1:2, expected dechlorination took place to form bis(organylthio)acetylenes (**1c**: R = Tol, 98%; **1e**: R = Pr, 48%) (scheme 7, II) (table III).

However, in the case of 1,2-bis(propylthio)-1,2-dichloroethylene **7a** (R = Pr) the reaction did not stop at this stage and a small amount of propyl butyl sulfide **12** was also isolated and characterized. Production of this sulfide can be explained by another trend



Scheme 7

of acetylenic chalcogenides R–C≡C–Y–R′, in which cleavage of the C–Y bond (Y = S, Se, Te) occurs in the presence of organometallics M–R″, to form metal acetylenide R–C≡C–M and organylchalcogenide R′–Y–R″ [7,37,45–48]. Here, part of BuLi reacts with acetylene **1e**, as shown in scheme 8.

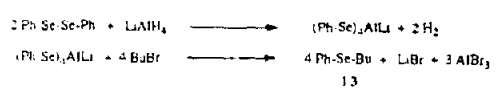


Scheme 8

• *Organylseleno compounds*

With 1,2-bis(phenylseleno)-1,2-dichloroethylene **8a**, in the same reaction conditions (**8a**/BuLi = 1:2), butyllithium does not react. Use of more drastic conditions (**8a**/BuLi = 1:4 and reflux) leads to complete disruption of the presumable intermediate bis(phenylseleno)acetylene **2b** to form only butyl

phenyl selenide **13** in 75% yield (scheme 7, I). It was unambiguously identified by spectroscopic methods, microanalysis and comparison with the reference selenide **13** prepared by the reaction of butyl bromide and benzeneselenolate (scheme 9). The latter was obtained by reduction of diphenyl diselenide with $LiAlH_4$, analogically to tellurolate preparation from diaryl ditelluride [19].



Scheme 9

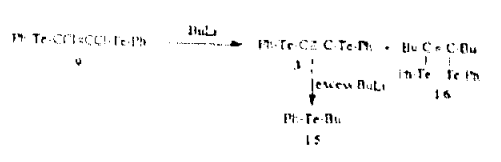
1,2-Bis(methylseleno)-1,2-dichloroethylene **8b** proceeds in a quite different fashion, as nucleophilic vinylic substitution of chlorine atoms (scheme 7, J). 5,6-Bis(methylseleno)dec-5-ene **14**, in 31% yield, was exclusively obtained in this reaction and identified by IR, ^1H NMR and mass spectra. It is worthwhile to note that in the mass spectrum, we failed to find peaks responsible for Me–Se–Bu and Me–Se–C≡C–Se–Me. This fact implies that dechlorination of dichloroethylene **8b** does not take place even to a minor extent.

Nucleophilic vinylic substitution of this kind is known both for unsubstituted haloethenes (for example, β-halostyrenes reacting with Me_2CuLi [50], or trihalostyrenes reacting with PhLi [39,51], or CF_2=CFCl reacting with BuCu [40]) and for polyhalovinyl ethers such as 1,2-difluoro-1-chlorovinyl ethers ROCF=CHF reacting with PhLi, BuLi, MeLi to substitute α-halogen [38,51]. But as was stated above, reaction of BuLi and trihalovinyl sulfides Bu–S–CF=CCl_2 leads to the acetylenic product Bu–S–C≡CH [38].

In conclusion, behavior of 1,2-bis(organylseleno)-1,2-dichloroethylene against BuLi depends on the nature of R. When R = alkyl, **8b**, substitution of chlorine atoms is a more favorable process than elimination, it is quite the reverse with R = aryl, **8a**.

• *Organyltelluro compounds*

Passing on to telluride, in a series of 1,2-bis(organyltelluro)-1,2-dichloroethenes **9** where Y = Te, drastically changes the reaction selectivity. All treatments of 1,2-bis(phenyltelluro)-1,2-dichloroethylene **9** with an excess of BuLi in THF, even at room temperature for 24 h, always lead to formation of a mixture as seen by TLC and HPLC (scheme 10).



Scheme 10

Expected bis(phenyltelluro)acetylene **3** was characterized by comparison with an authentic sample of acetylene **3** prepared by another method depicted in this paper, but the yield is very low (15%). In a second fraction, containing a small amount of acetylene **3**, two others products **15** and **16** were unambiguously identified. The presence in the ^1H NMR spectra of the mixtures of the signals of two different butyl groups at δ, ppm, 0.97t (3H), 1.55–1.67m (4H), 2.97–3.07t and 2.70t (2H), apart from the signals of the phenyltelluro group (7.77–7.83q, 7.30–7.43t, C_6H_5Te, A_2X_3 system), gives evidence that in this case, cleavage of the C–Te bond may produce butyl phenyl telluride PhTeBu **15** and probably substitution of chlorine atoms in dichloroethylene **9** takes place, to form 5,6-bis(phenyltelluro)dec-5-ene **16**. Mass spectrum of the mixtures confirms formation of Ph–Te–C≡C–Te–Ph **3** and Ph–Te–Bu **15**. Absence of the molecular ion for BuC(TePh)=C(TePh)Bu **16** however did not allow us to undeniably consider that this compound was not formed, since for selenides and tellurides there were known cases where a parent ion was too unstable to be detected [51]. Presence of a group of ions at m/z 434 (100) which could answer for both the polyisotopic molecular ion $[PhTeC{\equiv}CTePh]^+$ and the fragment ion $[M-2\ Bu]^+$ and a group of ions at m/z 414 (100) which could result from both PhTeTePh and $[M-Bu-Ph]^+$ speaks in favor of the existence of compound **16** in the reaction mixture. Besides, here were also found peaks of molecular and/or fragmental ions characteristic for other by-products: Ph–Te(O)C≡C–Te–Ph, Ph–Te–Te–Ph, Bu–Te–Te–Ph, $[Bu-(Te)C{=}CTe-Ph]^+$ or Bu–Te–C=C–Te–Ph. Formation of Ph–Te–Te–Ph in reaction was evidenced also by HPLC comparison with an authentic sample of diphenyl ditelluride. Butyl phenyl ditelluride is likely formed as a rearrangement product thanks to interaction of Ph–Te–Bu and Ph–Te–Te–Ph.

It could be concluded that in the case of 1,2-bis(phenyltelluro)-1,2-dichloroethylene **9**, reaction with BuLi is very complex and results in simultaneous dechlorination and cleavage of the C–Te bond in the intermediate Ph–Te–C≡C–Te–Ph **3** with butyllithium to form Ph–Te–Bu **15**, and also in substitution of chlorine atoms with a butyl group giving **16** (scheme 10).

Conclusion

Hence, we have found a new and general method to synthesize bis(organylthio)acetylenes **1**, bis(organylseleno)acetylenes **2**, bis(aryltelluro)acetylenes **3** in preparative yields by dehydrochlorination of the corresponding 1,2-bis(organylthio)chloroethylenes **4**, 1,2-bis(organylseleno)chloroethylenes **5**, 1,2-bis(aryltelluro)-chloroethylenes **6**, with KOH/DMSO. This method is the only one acceptable for all these three types of chalcogen-substituted acetylenes **1**–**3**. Besides, it is the only method that makes preparation of bis(aryltelluro)acetylenes **3** possible. The *tert*-BuOK–*tert*-BuOH system can also be used here, but only in the case of chloroethylenes **4** and **5**.

Only bis(organylthio)acetylenes **1** can be prepared also in preparative yields, by a similar method of dechlorination of 1,2-bis(organylchalcogeno)-1,2-dichloroethylenes **7**–**9** with BuLi, 1,2-dichloroethylene **9** giving a mixture of different products and 1,2-dichloroethylene **8** producing butyl aryl selenide **13**

in the case of aryl substituents in **8**, or 5,6-bis(methylselenenyl)dec-5-ene **14** in the case of alkyl substituents in **8**.

While the known reactions leading to the acetylenes **1–3** can be used mainly to prepare these acetylenes with alkyl substituents [7–13,14,17,20,21] only a few are known that are usable for aryl-substituted acetylenes **1**, **2** [16,18,19], but not for acetylenes **3**. The methods depicted here, which give acetylenes **1–3** in yields comparable to or better than those for the known methods, greatly expand the synthesis possibilities of acetylenes of this type.

Experimental section

IR spectra were recorded on a Biorad FTS 155 spectrometer. ^{1}H NMR spectra on a JEOL PMX 60 SI spectrometer at 60 MHz. Tetramethylsilane was used as internal reference. HPLC analyses were carried out on a chromatograph Spectra-Physics SP 8700 with a SP8440 XR UV/VIS detector and computing integrator SP4290, HPLC column SPHERI-5 ODS. Mass spectra of the individual compounds and mixtures of the products were obtained on a mass spectrometer Riber Nermag R10-10H, at electron energy 70 eV.

Preparation of chloro- and dichloroethylenes

1,2-Bis(propylthio)-1,2-dichloroethylene **7a**, 1,2-bis(tolylthio)-1,2-dichloroethylene **7b** were prepared from thiolate and tetrachloroethylene according to the known method [30] in 57% and 68% yields, respectively. 1,2-Bis(phenylseleno)-1,2-dichloroethylene **8a**, 1,2-bis(methylseleno)-1,2-dichloroethylene **8b**, 1,2-bis(phenyltelluro)-1,2-dichloroethylene **9** were prepared from dichalcogenides R–Y–Y–R (R = Me, Ph, Y = Se, R = Ph, Y = Te) and dichloroacetylene according to the known method [22–24] in 40%, 68% and 92% yields, respectively. 1,2-Bis(methylseleno)chloroethylene **5a** and 1,2-bis(phenylseleno)chloroethylene **5b** were prepared from diselenides R–Se–Se–R (R = Me, Ph) and chloroacetylene according to the known method [22,23] in 87% and 60% yields, respectively. Physicochemical constants, IR and ^{1}H NMR spectra, for all these compounds, are collected in table I.

• *1,2-Bis(phenylthio)chloroethylene* **4a**

0.5 mol of benzenethiol, an excess of $CHCl{=}CCl_2$ (1.3 mol) and 0.11 g of benzoyl peroxide, added in two portions, were refluxed in a pyrex flask for 22 h. Excess of $CHCl{=}CCl_2$ was stripped off and the residue was distilled in vacuo. Two main fractions were obtained: 62.7 g of a 82:18 mixture of phenyl 2,2-dichlorovinyl sulfide Ph–S–CH=CCl_2 **10** and phenyl 1,2-dichlorovinyl sulfide **11** with bp 88.5–110 °C (1 torr), n_D^{20} 1.6125; 15.5 g of pure chloroethylene **4a** with bp 184–186 °C (2 torr), n_D^{20} 1.6728 (HPLC purity 98%).

Found %: C 57.65, H 3.86, Cl 14.81, S 21.91. $C_{14}H_{11}ClS_2$. Calc %: C 60.31, H 3.98, Cl 12.72, S 23.00.

For IR and NMR spectra, see table I.

• *1,2-Bis(phenyltelluro)chloroethylene* **6**

Into a stirred solution of 6 g (11.6 mmol) of ditelluride PhTeTePh in 120 mL of dry, peroxide-free Et_2O in a pyrex reaction flask equipped for Vis-irradiation, a steady flow of chloroacetylene was introduced. Chloroacetylene was prepared by dropwise addition of 30 mL of a 1:1 mixture of *cis* and *trans*-CHCl=CHCl into a vigorously agitated solution of 1.5 g of triethyl benzyl ammonium chloride in 35 mL of 50% NaOH. Introduction of CH≡CCl was continued for 9 h. During the reaction the dark brown color of the Ph–Te–Te–Ph solution changed to light green. The reaction mixture thus obtained was left overnight. After distillation of Et_2O, the residue was dissolved in CH_2Cl_2 and traces of metallic Te produced during the reaction were filtered off. 6.73 g of chloroethylene **6** (93% purity according to HPLC) as an orange oil was obtained in 97% yield.

Found %: C 34.36, H 2.25, Cl 7.92, Te 53.06. $C_{14}H_{11}ClTe_2$. Calc %: C 35.79, H 2.36, Cl 7.54, Te 54.31.

For IR and NMR spectra, see table I.

Mass spectrum: polyisotopic molecular ion of chloroethylene **6** at *m/z* (abundance found/abundance calculated) 464 (36/15), 465 (31/14), 466 (59/33), 467 (54/25.5), 468 (100/62.5), 469 (59/31), 470 (100/97), 471 (72/20.5), 472 (86/100), 473 (56/15.5), 474 (54/64.5), 475 (27/10), fragment ion $PhTe^+$ at *m/z* 207 (100), fragment ion $[C_6H_4C_6H_4]^+$ at *m/z* 152, fragment ion $[C_6H_5C{\equiv}CH]^+$ at *m/z* 102. As admixture was also found polyisotopic molecular ion of ethyl 1-(phenyltelluro)ethyl ether, Ph–Te–CH(CH_3)OC_2H_5, at *m/z* 278 (50/77.5), 279 (75/66), 280 (100/100).

Preparation of bis(organylchalcogeno)acetylenes **3**

• *General conditions of dehydrochlorination of 1,2-bis(organylchalcogeno)chloroethylenes* **4–6**

(A) With tert-BuOK/tert-BuOH

A mixture of 21.5 mmol of the suitable chloroethylene, 150 mL of *tert*-BuOH and 21.5 mmol of *tert*-BuOK was heated at 50 °C and stirred for several hours. Excess of *tert*-BuOH was stripped off in vacuo and poured in 100 mL of water. After extraction by three portions of 30 mL of ether, drying and elimination of ether, the crude acetylenic product was purified by distillation or crystallization.

(B) With KOH/DMSO

Dehydrochlorination can be carried out at room temperature, by stirring a mixture of 5.8 mmol of chloroethylene and 5.8 mmol of KOH in 12 mL of DMSO. Dichloromethane was better for extraction. Specific conditions and yields for several chloroethylenes are presented in table II. Physicochemical constants and spectral characteristics of acetylenes **3** are given in table III.

• *General conditions of dechlorination of (E)-1,2-bis(organylthio)-1,2-dichloroethylene* **7**

At −55 °C under nitrogen atmosphere, 13.6 mmol of the suitable dichloroethylene in 200 mL of Et_2O was added during 1 h to a stirred mixture of 17 mL (27 mmol) 1.6 M BuLi in hexane and 50 mL Et_2O. Then the temperature was allowed to rise to 20 °C and stirring was continued during 8 h. The LiCl formed was filtered off. The residual Et_2O solution was washed with three portions of 30 mL of water and dried over $CaCl_2$. After evaporation of the solvents the residue was distillated or crystallized. IR and ^{1}H NMR spectra are gathered in table III.

From 1,2-bis(propylthio)-1,2-dichloroethylene **7a**, butyl propyl sulfide BuSPr **12** was isolated in 12% yield. Bp 20 °C (1 torr), n_D^{20} 1.4518 (lit [31] bp 167–168 °C, n_D^{22} 1.4510).

• *Interaction of 1,2-bis(phenylseleno)-1,2-dichloroethylene* **8a** *with butyllithium*

(A) Ratio 8a/BuLi = 1:2

1.07 g (10 mmol) of Ph–Se–CCl=CCl–Se–Ph **8a** in 250 mL Et_2O was treated with 12.5 mL (20 mmol) 1.6 M BuLi in hexanes. After stirring for 8.5 h at −55 °C and 10 h at 20 °C, usual work-up gave 3.94 g of unreacted Ph–Se–CCl=CCl–Se–Ph with mp 94–95 °C (EtOH) and 0.36 g of a mixture containing, according to HPLC, 95% of Ph–Se–CCl=CCl–Se–Ph **8a** and 2% of Ph–Se–Bu **13**.

(B) Ratio **8a** *: BuLi = 1:4*

To a stirred solution of 14.8 mL (23.7 mmol) 1.6 M BuLi in hexane and 100 mL Et_2O 4.07 g (10 mmol) of Ph-Se-CCl=CCl-Se-Ph **8a** in 150 mL Et_2O was added during 1 h at room temperature and under nitrogen atmosphere. 9.5 h later another 14.8 mL 1.6 M BuLi in hexane was introduced into the reaction mixture. Stirring was continued for 3 h. According to the TLC test, the reaction mixture contained only one product. This mixture was treated with 150 mL of water. The ether layer was separated, dried over $CaCl_2$. After evaporation of the solvents and distillation in vacuo, 3.26 g (75.5% yield) of butyl phenyl selenide, Ph-Se-Bu **13**, was obtained (93% purity according to HPLC). Bp 70-74 °C (0.8 torr), n_D^{20} 1.5600.

Found %: C 56.47, 56.43; H 6.96, 6.65; Se 37.21, 37.62. $C_{10}H_{14}Se$. Calc %: C 56.34; H 6.62; Se 37.04.

IR, ν, cm^{-1}: 3 071, 2 958, 2 928, 2 870, 1 579, 1 477, 1 461.

^1H NMR ($CDCl_3$, δ, ppm): 7.57q, 7.27t (5H, C_6H_5, A_2X_3, $^3J_{HH}$ 4 Hz), 2.87t (2H), 1.47m (4H), 0.93t (3H).

Lit [56]: bp 85 °C (3 torr).

Butyl phenyl selenide **13**, for identification, was prepared in an authentic way: 2 g (6.4 mmol) of diphenyl diselenide in 30 mL of THF were treated with 0.48 g (13 mmol) of $LiAlH_4$ under nitrogen atmosphere and then 1.76 g (12.8 mmol) of butyl bromide was introduced into the reaction mixture followed by 5 mL of HMPA. The mixture was stirred for 5 h, poured in 100 mL of water and extracted with diethyl ether. After drying over $CaCl_2$ and evaporation of Et_2O, 2.7 g (98%) of pure selenide **13** was obtained. Bp 75-76 °C, n_D^{20} 1.5561.

IR, cm^{-1}: 3 071, 2 959, 2 930, 2 873, 2 805, 1 580, 1 477, 1 462, 1 438, 1 379, 1 297, 1 259, 1 202s, 1 071, 1 024, 985s, 901, 736s, 690, 670, 485, 467, 456.

Lit [56]: n_D^{20} 1.5589.

• *Interaction of 1,2-bis(methylseleno)-1,2-dichloroethylene* **8b** *(R = Me) with BuLi*

(A) Ratio **8b** *: BuLi = 1:2*

At -50 °C under nitrogen atmosphere 5 g (17.7 mmol) of Me-Se-CCl=CCl-Se-Me **8b** in 75 mL Et_2O was treated analogously with 22.8 mL (36.4 mmol) 1.6 M BuLi in hexane for 1 h and then for 8 h at room temperature. According to TLC the reaction mixture contained only the parent compound. After usual workup, 2.54 g of the starting material was recovered.

(B) Ratio **8b** *: BuLi = 1:4*

At room temperature 2.54 g (8.75 mmol) of Me-Se-CCl=CCl-Se-Me **8b** in 50 mL Et_2O was introduced under nitrogen flow into a solution of 11.5 mL (18.4 mmol) 1.6 M BuLi (in hexanes) and 25 mL Et_2O. The reaction mixture was stirred for 6 h and then another portion of 11.5 mL 1.6 M BuLi was added. Stirring was continued for 18 h and the reaction mixture was quenched with H_2O. The water layer was extracted with Et_2O (50 mL) and CH_2Cl_2 (50 mL). Combined extracts were treated with $NaHCO_3$ and NaOH and dried over $CaCl_2$. After evaporation of the solvent, 0.91 g (31%) of 5,6-bis(methylseleno)deca-5-ene Bu-C(SeMe)=C(SeMe)-Bu **14** was obtained. n_D^{20} 1.[illegible]

IR spectrum, ν, cm^{-1}: 2 959, 2 927, 2 873, 1 462, 1 425, 1 379, 1 267, 1 201, 908, 775, 648.

^1H NMR ($CDCl_3$), δ, ppm: 1.978 (3H, CH_3-Se), 2.56 (2H, CH_2), 1.6-1m, 1.25m (4H, C_2H_4), 0.92t (3H, CH_2-CH_3).

Mass spectrum: polyisotopic molecular ion (M) [illegible] (relative intensity): 422 (74), 423 (59), 424 (87), 425 (46), 426 (97), 427 (44), 428 (100), 429 (55), 430 (65), 431 (68), 432 (91).

• *Interaction of 1,2-bis(phenyltelluro)-1,2-dichloroethylene* **9** *with BuLi*

Under a nitrogen atmosphere, 3.33 g (6.6 mmol) of Ph-Te-CCl=CCl-Te-Ph **9** was introduced into a mixture of 8.5 mL (13.6 mmol) 1.6 M BuLi (in hexanes) and 20 mL THF. After stirring for 14 h, solvents were evaporated and the residue was extracted twice with 30 mL of CH_2Cl_2. Extracts were dried over Na_2SO_4. After evaporation of methylene chloride, 2.95 g of a mixture containing the starting dichloroethylene **9** and products, were obtained.

^1H NMR, δ, ppm: 7.83q, 7.30t (C_6H_5, A_2X_3), 3.07t, 2.70t, 2.67m, 0.97dt.

Separation by column chromatography (silica gel, cyclohexane/CH_2Cl_2, 95:5) gave only 1.65 g of the initial product mixture and 0.58 g (20%) of Ph-Te-C≡C-Te-Ph **3** identified by TLC by comparison with a sample of this acetylene obtained in another way. From mass spectrum of the product mixture, it was evidenced that besides Ph-Te-C≡C-Te-Ph **3** which gave a polyisotopic molecular ion at m/z (relative abundance found/relative abundance calculated) 438 (45/50), 437 (31/14), 436 (87/93), 435 (18/15), 434 (100/100), 432 (62/67), 431 (31/27), 430 (18/46), 429 (12/16), 428 (12/16), this mixture contained PhTeBu **15** [m/z 262 (100/100)] and probably Ph-Te-C(Bu)=C(Bu)-Te-Ph **16** that appeared in the spectrum only as the fragment ions $[PhTeC_2TeBu]^+$ at m/z 414 and $[Te_2C_2Bu]^+$ at m/z 336.

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