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Synthesis of α-phenylchalcogeno acetic acids, ethyl-α-phenylchalcogeno acetates and ethyl-α-halo-α-phenylchalcogeno acetates

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Abstract

Reaction of phenyltellurolate or phenylselenolate anion with α-bromoacetic acid under phase transfer conditions using a liquid–solid system affords the α-phenyltelluro acetic acid and the α-phenylseleno acetic acid in 44 and 50% yields respectively. Under similar reaction conditions, phenyl chalcogenate anions react with ethyl α-bromoacetate to give the corresponding ethyl-α-phenyltelluro acetate in 52% and ethyl-α-phenylseleno acetate in 47% yield.

Reaction of phenylselenenyl chloride with ethyl diazoacetate in THF at 0°C yields exclusively the ethyl-α-chloro-α-phenylseleno acetate in 88% yield. Similar reactions performed by addition of phenylselenenyl bromide in THF or benzene to the ethyl diazoacetate at different temperatures result in mixtures of ethyl-α-bromo-α-phenylseleno acetate and ethyl-α,α-bis(phenylseleno) acetate in different ratios. However, when the ethyl diazoacetate was slowly added to a solution of phenylselenenyl bromide in benzene under reflux, the ethyl-α-bromo-α-phenylseleno acetate was obtained in 84% yield as the only product. Reaction of ethyl diazoacetate with phenyltellurenyl bromide in benzene at room temperature results in formation of ethyl-α-bromo-α-phenyltelluro acetate that decomposes rapidly into the corresponding tellurone.

Addition of ethyl diazoacetate to a mixture of diphenyldiselenide and copper sulfate in benzene under reflux results in a mixture of ethyl-α-phenylseleno acetate: ethyl-α,α-bis(phenylseleno) acetate (10:1). Using an alternative route, the ethyl-α-phenylseleno acetate was obtained in 74% yield by esterification of α-phenylseleno acetic acid in benzene with ethanol/sulfuric acid. The ethyl-α-phenylseleno acetate was transformed into the ethyl-α-bromo-α-phenylseleno acetate in 41% yield by treatment with N-bromosuccinimide.

On the other hand, the copper-catalyzed thermal reaction of ethyl diazoacetate with diphenyl ditelluride in benzene afforded the corresponding ethyl-α-phenyltelluro acetate as the only product.

1. Introduction

Few methods to obtain α-telluro carbonyl compounds have been reported in the literature [1,2]. Huang *et al.* [3] described an efficient and easy synthesis of α-phenyltelluroesters through the Reformatsky reaction using electrophilic tellurenyl iodides. The other available method for obtaining α-organyltelluro esters is that recently developed by Silks *et al.* [2] employing tellurolate anions and α-bromoesters. The same work presents the first report of the hydrolysis of ethyl-α-phenyltelluro acetate with LiOH in THF/H_2O to the phenyltelluro acetic acid. In previous works, different tellurolate reagents were used to remove α-substituents of α-haloketones [4,5] and α-halo carboxylic acids [4,6], but no substitution products were obtained.

In contrast, many preparative methods have been described for the synthesis of analogous α-seleno carbonyl compounds [7–17]. Dianions generated from α-phenylseleno carboxylic acids with LDA were used in syntheses of natural products [18].

Recently we described the reaction of phenylselenenyl bromide with ethyldiazo acetate in THF at 0°C, to give a mixture of ethyl-α-bromo-α-phenylseleno acetate and ethyl-α-α-bis(phenylseleno) acetate. This mixture

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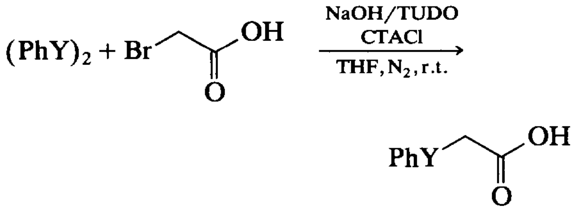
was used to generate a selenium stabilized carbenium ion under Friedel–Crafts conditions in reaction with aromatic compounds [19]. The formation of a C–C bond and the increment of a two carbon unit containing an acyl group with an α-selenium group into an aromatic ring occurs easily owing to the stabilization of carbenium ions by the selenium atom [19,20].

Ethyl-α,α-bis(phenylseleno) acetate was obtained previously by the Se–Se insertion reaction when ethyl diazoacetate was allowed to react with diphenyl diselenide in presence of copper-bronze alloy or $BF_3 \cdot Et_2O$ as catalyst [21]. However, detailed synthesis of the pure ethyl α-bromo-α-phenylseleno acetate has not been previously reported. Analogous tellurium derivatives are unknown. In view of our interest in the synthetic applications of ethyl-α-phenylchalcogeno acetates and the corresponding carboxylic acids, we want to disclose in this paper new methods to synthesize these species. Further investigations on synthetic applications of these compounds are now in progress.

2. Results and discussion

2.1. *α-Phenylchalcogeno acetates and α-phenylchalcogeno carboxylic acids under phase transfer conditions*

Nucleophilic substitution on the α-bromo acetic acid, using the sodium phenyltellurolate and sodium phenylselenolate anions generated *in situ* from the diphenyl dichalcogenide in a solid–liquid system, gives under phase transfer conditions the corresponding α-phenyltelluro acetic acid **I** and the new α-phenylseleno acetic acid **II** in 44 and 50% yields respectively (eqn. (1)).



(1)

Y = Te (**I**) 44%
Y = Se (**II**) 50%

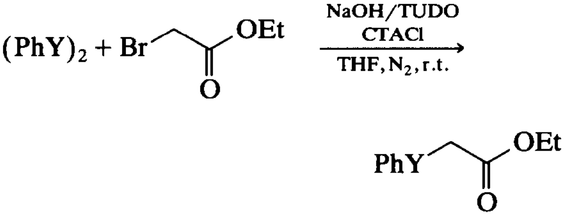
In these cases, powdered sodium hydroxide was used to cleave the Te–Te or Se–Se bond and thiourea dioxide (TUDO) was used as a reducing agent [22]. Cetyltrimethylammonium chloride (CTACl) was used as phase transfer catalyst, where others such as 2 HT-75 (a trade name for a mixture of dialkyldimethylammonium chlorides (85% n-C_{18} and 15% n-C_{16} [23]) or cetyltrimethylammonium bromide (CTAB) gave poorer results.

α-Phenyltelluro acetic acid **I** is unstable in solution but very stable in the solid state. This compound was obtained as a yellow solid, m.p. 94–95°C (92–94°C lit. [2]), which could be stored for several months without decomposition.

A minor amount of acetic acid was detected by ^{1}H NMR in the crude products in both reactions. This by-product formation occurs by reductive cleavage of the C–Br bond in the starting material or of the C–chalcogen bond in the product promoted by a chalcogenate anion. It is worthy of mention that when using a liquid–liquid PTC system(organic-aqueous), the α-chalcogeno acetic acids were not obtained.

The advantage of our liquid–solid phase transfer procedure is that the phenyltelluro acetic acid (**I**) is obtained in a one-pot reaction from bromoacetic acid, while the Silks procedure requires the synthesis of ethyl-α-phenyltelluro acetate that is further hydrolyzed to **I** by reaction with LiOH [2].

Use of ethyl-α-bromo acetate instead of the α-bromo acetic acid under the same reaction conditions in the reaction with the diphenyl dichalcogenide gave the corresponding α-phenyl chalcogeno esters **III** and **IV** in 52 and 41% yield (eqn. (2)).

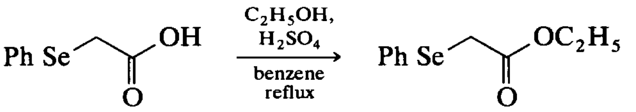


(2)

Y = Te 52% (**III**)
Y = Se 41% (**IV**)

Attempts to obtain secondary α-seleno and α-telluro acids or the corresponding esters were not successful, since the reductive removal of halogen atom was the preferred reaction. We also found that reaction of the lithium butyl tellurolate generated by insertion of elemental tellurium into the carbon–lithium bond of butyl lithium [24] with α-bromo acetic acid in THF using a different order of addition results only in the acetic acid and no substitution product was formed.

Alternatively, compound **IV** was easily and cleanly obtained in 74% yield by reaction of **II** with ethanol/sulfuric acid in benzene (eqn. (3)). The water formed was removed with a Dean-Stark trap and the reaction was complete after 3 h under reflux.



(**IV**)

(3)

2.2. *Ethyl-α-halogen-α-phenylchalcogeno acetates*

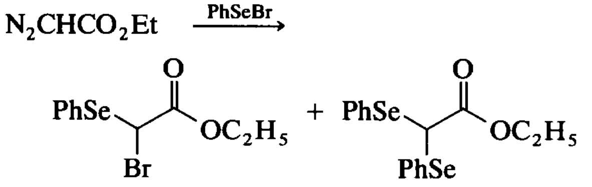
Insertions of diazoester into the chalcogen–halogen bond have been reported previously by us [19] and by other authors [25]. The reaction of ethyl-2-diazo-3-methyl butanoate with phenylselenenyl iodide generated *in situ* produced a vinyl selenide indicating that dehydrohalogenation occurs readily under the conditions used [25]. In our previous communication [19] we remarked that addition of phenylselenenyl bromide in THF to a solution of ethyldiazoacetate in THF at 0°C yields a mixture of **V** and **VI** (eqn. (4)) in a ratio of 1.5 : 1. We describe here an improvement of this reaction and of the reaction of ethyl diazoacetate with diphenyldichalcogenides.

Reaction of diazomethane with phenylselenenyl bromide at −78°C is known to give the product of insertion of diazomethane into the Se–Br bond, but at higher temperatures this reaction leads to the bis(phenylseleno) acetal as by-product [26]. We have observed that the reaction of ethyl diazoacetate with phenylselenenyl bromide below 0°C gives a mixture of **V** and **VI** (eqn. (4), Table 1) and the product ratio is dependent on the order of addition. When ethyl diazoacetate was added to a solution of phenylselenenyl bromide in THF at −78°C, the mixture of **V** and **VI** was obtained (eqn. (4)), with **V** as the major component (1.2 : 1). Addition of the phenylselenenyl bromide to the diazoester in THF at −78°C gives the diseleno derivative **VI** as the major component (1 : 2 ratio). Performing this reaction at higher temperatures improves the formation of **V**, in contrast to what is observed [26] in reactions of diazomethane and PhSeBr. On the other hand, better results were obtained using benzene as solvent. These results are summarized in Table 1.

TABLE 1. Effects of temperature and of solvent on product ratio of reaction of ethyl diazoacetate and phenylselenenyl bromide

Temperature of reaction	Solvent	Ratio [a] of V:VI
−78°C	THF [b]	1:2
−78°C	THF [c]	1.2:1
0°C	Benzene [b]	2.5:1
0°C	THF [b]	1.5:1
0°C	CH_2Cl_2 [b]	1.5:1
r.t.	Benzene [b]	3.5:1
r.t.	THF [b]	2:1
reflux	Benzene [b]	10:1
reflux	THF [b]	5.7:1
reflux	Toluene [b]	8:1

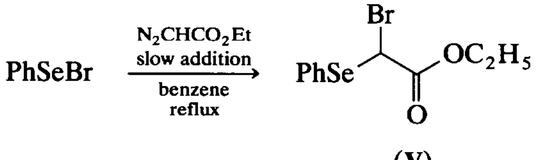
[a] Ratios determined by ^1H NMR spectra of crude products.
[b] Addition of PhSeBr to the diazoester.
[c] Addition of diazoester to the PhSeBr.



(V) (VI)

(4)

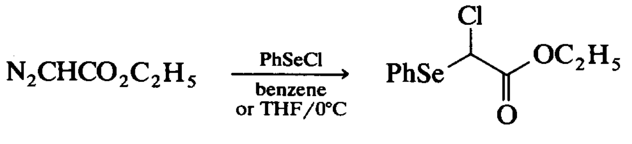
When ethyl diazoacetate was slowly added to a refluxing solution of phenyl selenenyl bromide in benzene, the halogenated compound **V** was obtained as the only product in 89% yield (eqn. (5)).



(V)

(5)

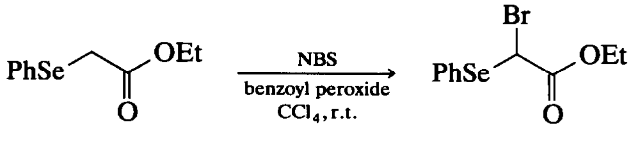
As discussed above, to obtain the insertion product alone when using phenylselenenyl bromide, solvent, temperature and order of addition are crucial. However, the reaction of ethyl diazoacetate with phenylselenenyl chloride gives only ethyl-α-chloro-α-phenylseleno acetate **VII** when the reaction is performed in THF or benzene even at 0°C (eqn. (6)). These results show that the nature of the halogen atom also plays an important role in determining the course of the reaction.



(VII)

(6)

We devised an alternative route to compound **V**. Reaction of ethyl-α-phenylseleno acetate with N-bromosuccinimide in presence of benzoyl peroxide using carbon tetrachloride as solvent gives the desired ethyl-α-bromo-α-phenylseleno acetate **V** in 41% yield (eqn. (7)).

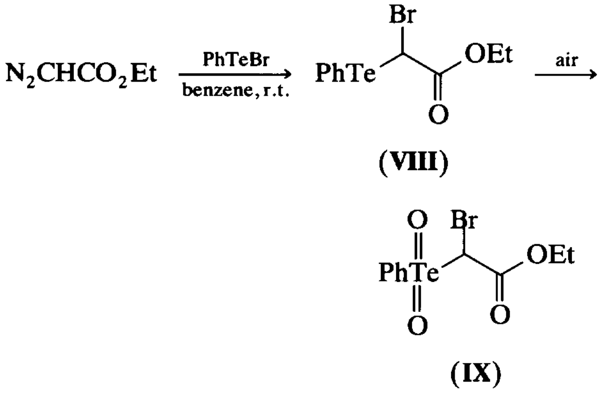


41%

(7)

Addition of ethyl diazoacetate to a solution of phenyltellurenyl bromide in benzene at room temperature results in the unstable ethyl-α-bromo-α-phenyltelluro acetate **VIII** (eqn. (8)). This result was not altered when the order of addition was reversed. Compound **VIII** was detected immediately after extraction, by ^1H

NMR and GC/MS, but in the presence of air it decomposes rapidly into a very insoluble white solid, tentatively characterized as the tellurone **IX**.



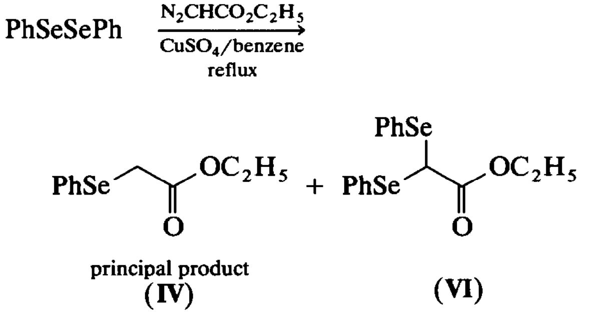
(VIII)

(IX)

(8)

2.3. *Copper sulfate-catalyzed reactions of diphenyl dichalcogenides with ethyl diazoacetate*

The slow addition of excess ethyl diazoacetate to a mixture of diphenyl diselenide and anhydrous $CuSO_4$ in benzene at reflux results in the formation of the ethyl-α-phenylseleno acetate **IV** and the ethyl-α,α-bis(phenylseleno) acetate **VI** in 74 and 6% yields, respectively (eqn. (9)). The products were separated by flash chromatography. Using equimolar amounts of reagents, significant quantities of diselenide were recovered and the mixture of **IV** and **VI** was obtained in a 1:2 ratio determined by ^{1}H NMR.



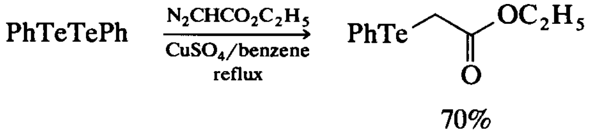
(IV)

(VI)

(9)

When the reaction was performed with the addition order of reagents reversed, unreacted diphenyl diselenide was recovered. The copper-catalyzed decomposition of ethyl diazoacetate with $CuSO_4$ under these reaction conditions probably occurs very rapidly and before reaction with the diselenide. No product was observed in the absence of $CuSO_4$ under several different reaction conditions.

When a mixture of diphenyl ditelluride and $CuSO_4$ in benzene was treated with ethyl diazoacetate, the corresponding α-phenyltelluro ester **III** was obtained in good yield (eqn. (10)). In this case no ditelluro derivative analogous to **VI** was detected.



(10)

3. Experimental section

3.1. *General*

Infrared spectra were obtained on a Perkin-Elmer 1600 Series FTIR spectrophotometer. ^{1}H NMR spectra were obtained on a Varian EM 360 L or Brüker AC-80 MHz spectrometer, with tetramethylsilane as the standard. Mass spectra were obtained on a Hewlett-Packard 5890 GC/MS system mass spectrometer at 70 eV. Elemental analyses were performed in a Perkin-Elmer 2400 CHN analyzer. All solvents were distilled before use. Reactions were monitored by thin-layer chromatography using Merck silica gel 60F-254 on alumina prepared plates. Flash chromatography was carried out on Merck silica gel 60 (230–400 mesh ASTM). Phenyl selenenyl chloride [27], phenyl selenenyl bromide [28], diphenyl diselenide [9] and diphenyl ditelluride [29] were obtained by previously described procedures. Anhydrous $CuSO_4$ was obtained by treatment of $CuSO_4 \cdot 5H_2O$ in a muffle furnace at 250°C for 5 h and stored in a vacuum desiccator.

3.2. *α-Phenyltelluro acetic acid (I) under phase transfer conditions*

A mixture of thiourea dioxide (0.42 g, 4 mmol), CTACl (0.24 g), sodium hydroxide powder (15 g), diphenyl ditelluride (1.636 g, 4 mmol) and THF (50 ml) was vigorously stirred under nitrogen at room temperature for 1 h. After this time bromoacetic acid (1.68 g, 12 mmol) in THF (10 ml) was added and the reaction mixture stirred for an additional 15 min at room temperature. The mixture was poured into cooled water (100 ml) and extracted with ethyl ether (3 × 40 ml portions). The organic layer was dried over $MgSO_4$ and evaporated to give unreacted diphenyl ditelluride. The aqueous layer was then acidified with 2 M hydrochloric acid and extracted with diethyl ether (3 × 30 ml portions) and with dichloromethane (3 × 30 ml portions). The combined organic layer was dried over $MgSO_4$ and filtered. The product shows a tendency to decompose on standing in solution and in the presence of air, giving diphenyl ditelluride as one of the decomposition products.

After removal of solvents under vacuum, recrystallization from petroleum ether of the obtained solid residue gave a stable yellow crystalline solid, identified as the α-phenyltelluro acetic acid. Yield: 0.93 g (44%). m.p. 94–95°C (lit. [2] = 92–94°C). ^{1}H NMR (C_3D_6O/TMS) δ(ppm) 3.53 (s, 2H) 7.18–7.39 (m, 3H) 7.75–7.95 (m, 2H) 8.65 (br s, 1H). Anal. Found: C, 36.78; H, 3.01. $C_8H_8O_2Te$ calcd.: C, 36.41; H, 3.03%. Mass spectrum m/e 264 (M^+).

3.3. α-Phenylseleno acetic acid (II) under phase transfer conditions

The procedure described above, when using diphenyldiselenide (1.26 g, 4 mmol), afforded after the reaction work-up the α-phenylseleno acetic acid (**II**) as a yellow oil. Yield: 0.86 g (50%). ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 3.46 (s, 2H) 7.18–7.35 (m, 3H) 7.48–7.67 (m, 2H) 9.00 (br s, 1H) mass spectrum m/e 216 (M^+). IR: 1702s cm^{-1}, 3056m cm^{-1}. Anal. Found: C, 44.41; H, 3.69; $C_8H_8O_2Se$ calcd.: C, 44.65; H, 3.72%.

3.4. Ethyl-α-phenyltelluro acetate (III) under phase transfer conditions

A mixture of thiourea dioxide (0.42 g, 4 mmol), CTACl (1.20 g), sodium hydroxide powder (15 g), diphenyl ditelluride (1.636 g, 4 mmol) and THF (50 ml) was vigorously stirred under nitrogen for 1 h. After this time, ethyl bromoacetate 2.00 g, 12 mmol) was added and the reaction mixture stirred for an additional 25 min at room temperature. The mixture was poured into cooled water (100 ml) and extracted with ethyl acetate (4 × 40 ml portions). The organic layer was washed with water, dried over $MgSO_4$ and evaporated. Purification by flash chromatography using hexane/ethyl acetate (8/2) as eluent afforded a yellow oil, identified as the ethyl-α-phenyltelluro acetate. Yield: 1.21 g (52%). ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 1.16 (t, J 7, 3H) 3.52 (s, 2H) 4.08 (q, J 7, 2H) 7.09–7.38 (m, 3H) 7.75–7.82 (m, 2H). IR 1716s cm^{-1}, 1570m cm^{-1}, 1362m cm^{-1}, 1250s cm^{-1} in accordance with the literature [2].

Mass spectrum m/e 294 (M^+). Anal. Found: C, 41.53; H, 4.22; $C_{10}H_{12}O_2Te$ calcd.: C, 41.15; H, 4.11%.

3.5. Ethyl-α-phenylseleno acetate (IV) under phase transfer conditions

The procedure as above, when using diphenyl diselenide (1.26 g, 4.0 mmol) afforded after purification the ethyl-α-phenylseleno acetate (**IV**) as a yellow oil. Yield: 0.8 g (41%). ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 1.16 (t, J 7, 3H) 3.46 (s, 2H) 4.05 (q, J 7, 2H) 7.08–7.36 (m, 3H) 7.41–7.66 (m, 2H).

3.6. Ethyl-α-phenylseleno acetate IV by esterification of II

Ethanol (0.92 g, 1.1 ml) and five drops of concentrated sulfuric acid were added to a round bottomed flask equipped with a reflux condenser and a Dean-Stark trap containing a solution of **II** (0.45 g; 2.1 mmol) in dry benzene (20 ml). The reaction mixture was refluxed for 3 h, then allowed to reach room temperature and washed with water (3 × 30 ml portions). The organic layer was dried over $MgSO_4$ and the solvent removed under vacuum. The product was purified by flash chromatography using hexane/ethyl acetate (8/2) as the eluent. The ethyl-α-phenylseleno acetate (**IV**) was obtained as a yellow liquid. Yield: 0.38 g (74%). Their IR and ^{1}H NMR spectra were identical with those of the product obtained in 3.5.

3.7. Ethyl-α-bromo-α-phenylseleno acetate (V)

3.7.1. From reaction of IV with N-bromosuccinimide

N-Bromosuccinimide (0.214 g; 1.2 mmol) and a catalytic amount of benzoyl peroxide (*ca.* 10 mg) were added to a solution of compound **IV** (0.29 g, 1.2 mmol) in carbon tetrachloride (4 ml) at room temperature. The reaction mixture was stirred at this temperature for 1 h 50 min, then diluted with dichloromethane (*ca.* 25 ml) and filtered through Celite. The filtrate was washed with water (3 × 25 ml portions), dried over $MgSO_4$ and the solvent removed under vacuum. The residue was purified by flash chromatography using hexane/ethyl acetate (8/2) as eluent. The ethyl-α-bromo-α-phenylseleno acetate V was obtained in pure form as a yellow liquid. Yield: 0.158 g (41%). Their IR, mass and ^{1}H NMR spectra were identical with those of product obtained in 3.7.2.

3.7.2. From reaction of PhSeBr and ethyldiazoacetate

To a solution of PhSeBr (0.236 g, 1.0 mmol) in dry benzene (6 ml) under reflux, ethyl diazoacetate (0.11 ml, 1.1 mmol) in dry benzene (4 ml) was added dropwise during 10 min. After addition was complete, the reaction mixture was refluxed for an additional 30 min, allowed to reach room temperature, diluted with ethyl acetate (*ca.* 40 ml) and washed with water (3 × 30 ml portions). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under vacuum to give the pure compound (**V**) as shown by its ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 1.21 (t, J 7, 3H) 4.15 (q, J 7, 2H) 5.4 (s, 1H) 7.1–7.4 (m, 3H) 7.5–7.8 (m, 2H). Yield: 0.289 g (89%). Mass spectrum m/e: 322 (M^+); IR: 1736 cm^{-1}.

3.8. Ethyl-α-chloro-α-phenylseleno acetate VII

A solution of phenylselenenyl chloride (0.191 g, 1.0 mmol) in THF (4 ml) was added dropwise at 0°C to a solution of ethyl diazoacetate (0.11 ml, 1.1 mmol) in THF (6 ml). A rapid disappearance of the red color was observed. After 25 min of stirring at 0°C, the THF was evaporated to give the pure compound (**VII**) as shown by its ^1H NMR ($CDCl_3$/TMS) δ (ppm) 1.22 (t, *J* 7, 3H) 4.16 (q, *J* 7, 2H) 5.50 (s, 1H) 7.2–7.5 (m, 3H) 7.6–7.8 (m, 2H). Mass spectrum *m/e* (M^+) 278. IR: 1744 cm^{-1}. Yield: 0.245 g (88%). Further purification of compound **VII** was accomplished by flash chromatography using hexane/ethyl acetate (8/2) as eluent. Anal. Found: C, 43.70; H, 4.18. $C_{10}H_{11}O_2SeCl$ calcd.: C, 43.24; H, 3.96%.

3.9. Ethyl-α-phenylseleno acetate (IV) from reaction of PhSeSePh with ethyl diazoacetate

A solution of ethyl diazoacetate (0.6 ml, 6 mmol) in benzene (10 ml) was added dropwise during 2 h to a mixture of anhydrous $CuSO_4$ (0.2 g) and diphenyl diselenide (0.314 g, 1 mmol) in benzene (6 ml) under reflux. After the end of addition, the reaction mixture was refluxed for an additional half hour, allowed to reach room temperature, diluted with ethylacetate (40 ml) and washed with brine (3 × 30 ml portions) and water (2 × 30 ml portions). The organic layer was dried over $MgSO_4$, filtered and evaporated to give a mixture of compounds **VI** and **IV** (major component) as indicated by the ^1H NMR spectrum of the residue.

The residue was purified by flash chromatography using hexane/ethyl acetate (8/2) as eluent. The ethyl-α-phenylselenoacetate **IV** was obtained as a yellow oil. Yield: 0.36 g (74%). Their ^1H NMR and mass spectra were identical with those of the product obtained under PTC.

3.10. Ethyl-α-phenyltelluro acetate (III) from reaction of PhTeTePh with ethyl diazoacetate

A solution of ethyl diazoacetate (0.4 ml, 4 mmol) in benzene (10 ml) was added dropwise during 2 h to a mixture of anhydrous $CuSO_4$ (0.2 g) and diphenylditelluride (0.409 g, 1 mmol) in benzene (6 ml) under reflux. After the end of addition, the reaction mixture was refluxed for an additional half hour, allowed to reach room temperature, diluted with ethyl acetate (*ca.* 40 ml) and washed with brine (3 × 30 ml portions) and water (2 × 30 ml portions). The organic phase was dried over $MgSO_4$, filtered and evaporated to give compound **III** as indicated by the ^1H NMR spectrum of the residue. Flash chromatographic purification was accomplished using hexane/ethyl acetate (9/1) as eluent. The ethyl-α-phenyltelluro acetate **III** was obtained as a yellow oil. Yield: 0.41 g (70%). Their ^1H NMR and mass spectra were identical with those of the product obtained under PTC.

3.11. Reaction of PhTeBr with ethyl diazoacetate

A solution of ethyl diazoacetate (0.22 ml, 2.2 mmol) in benzene (5 ml) was added dropwise during 10 min at room temperature to a solution of phenyltellurenyl bromide (prepared by adding 0.16 g (1.0 mmol) of bromine in benzene (*ca.* 5 ml) to the diphenyl ditelluride (0.409 g; 1.0 mmol) in THF (5 ml) at 0°C under nitrogen atmosphere). After the end of addition the reaction mixture was stirred for an additional 30 min at room temperature. A gradual disappearance of the dark red color of the reaction mixture was observed. The resulting yellow solution was diluted with ethyl acetate (*ca.* 40 ml) and washed with brine (3 × 30 ml portions) and water (2 × 30 ml portions). The organic phase was dried over $MgSO_4$, the solvent removed under vacuum and the residue was immediately analyzed by ^1H NMR (CCl_4/TMS) δ (ppm) 1.36 (t, *J* 7, 3H) 4.36 (q, *J* 7, 2H) 4.65 (s, 1H) 7.4–7.7 (m, 3H) 8.0–8.5 (m, 2H) CG/MS. *m/e* 372 (M^+). The obtained product decomposed rapidly into a white solid, which was washed with carbon tetrachloride (5 × *ca.* 10 ml portions) and with chloroform (2 × *ca.* 10 ml portions). The insoluble white solid was characterized as the tellurone IX. Yield: 0.62 g (77%). Anal. Found: C, 29.41; H, 2.42. $C_{10}H_{11}TeBrO_4$ calcd.: C, 29.80; H, 2.73%.

Acknowledgments

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