

The Reaction of Diaryliodonium-2-carboxylates with Diaryl Ditellurides, Diaryl Diselenides, or Diaryl Selenaditellurides

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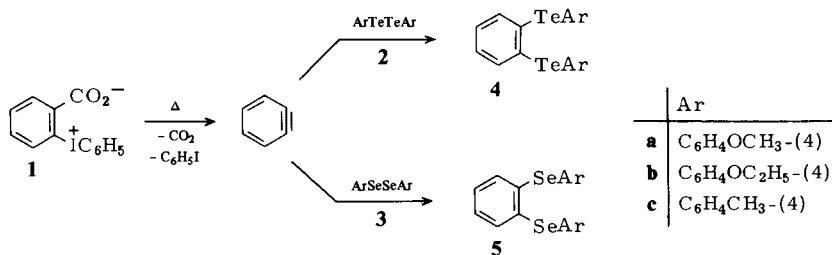
The title reaction, which yields the respective *ortho*-heterodisubstituted phenylene derivatives (**4**, **5**, **14**, **15**), has been further investigated. The present results substantiate our previously postulated mechanism involving the intermediacy of singlet benzyne.

Umsetzung von Diaryliodonium-2-carboxylaten mit Diarylditelluriden, Diaryldiseleniden oder Diarylselenaditelluriden

Die Titelreaktion, bei welcher die entsprechenden *o*-heterodisubstituierten Phenylenabkömmlinge (**4**, **5**, **14**, **15**) entstehen, wurde erneut untersucht. Die jetzigen Ergebnisse bestätigen unseren früher vorgeschlagenen Mechanismus mit Benzyn im Singulett-Zustand als Zwischenstufe.

Introduction

In an earlier report¹⁾, we described the reaction between 2-(phenyliodonio)benzoate (**1**) and diaryl ditellurides **2** or diselenides **3**, which resulted in the formation of the respective *ortho*-disubstituted derivatives **4** or **5**.



In this prior work, we postulated the intermediacy of benzyne, which undergoes concerted insertion into the Te–Te or Se–Se bond. Nevertheless, we made mention of the fact that the reaction was not entirely reproducible, frequently leading to ill-defined products of low heteroatom content. In the present work, we report more detailed investigations of this reaction which bear on the inconsistent results previously obtained, the applicability of the reaction to other derivatives of Selenium and Tellurium, and the mechanism involved.

¹⁾ N. Petraghani and V. G. Toscano, Chem. Ber. 103, 1652 (1970).

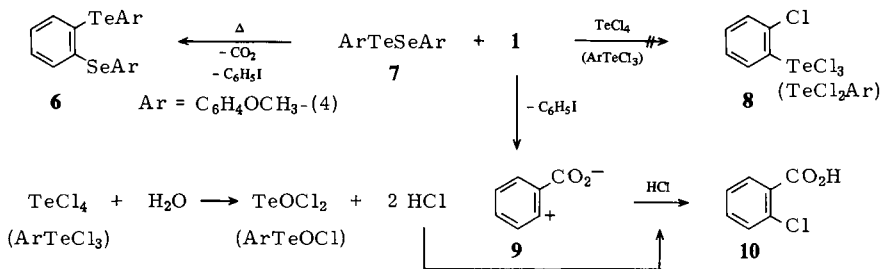
Results and Discussion

It is known that the decomposition of iodonium salts, as well as the types of products formed, are markedly influenced by the presence of heavy metals, which probably promote decomposition *via* radical mechanisms²⁻⁵). Theorizing that the inconsistent results obtained in our earlier work might be attributable to such impurities, present in the iodonium salt, we purified the salt by recrystallization from water in the presence of EDTA. The composition of the iodonium salt purified in this manner corresponded to that of the monohydrate and exhibited m.p. 220–222°C⁶). When this salt was employed in the reaction with bis(4-ethoxyphenyl) ditelluride, the desired product was obtained with reproducible yields, permitting a more detailed study of the scope and applicability of the reaction. Thus, bis(4-methoxyphenyl) and di-*p*-tolyl ditellurides reacted to give **4a** and **c** in yields of ca. 50%. Similarly, bis(4-methoxyphenyl) diselenide yielded **5a** (18%), and bis(4-methoxyphenyl) selenaditelluride (**7**) yielded the corresponding compound **6** (26%).

In contrast, diphenyl ditelluride and di-2-naphthyl ditelluride were unreactive (50–75% recovery of starting ditelluride).

Considering the electrophilic character of benzyne, this lack of reactivity relative to the methoxy- and methyl-substituted analogues might be rationalized in terms of the electron donating properties of these substituents and the consequent enhancement of the electron density of the Te–Te bond.

We also investigated the reaction of **1** with tellurium tetrachloride and aryltellurium trichlorides, expecting to obtain the corresponding *ortho*-halotellurium derivative **8**. These reactions may be viewed on the basis of electrophilic addition of tellurium to benzyne (benzyne exhibits both electrophilic and nucleophilic character), analogous to that observed in the addition of the halides of Hg, Sn, Si, P, and Cu^{7,8}) and of tellurium halides to olefines⁹).



²) M. C. Caserio, D. L. Glusker, and J. D. Roberts, *J. Am. Chem. Soc.* **81**, 336 (1959).

³) F. M. Beringer and P. Bodlaender, *J. Org. Chem.* **34**, 1981 (1969).

⁴) F. M. Beringer and S. J. Huang, *J. Org. Chem.* **29**, 445 (1964).

⁵) L. Friedman, *J. Am. Chem. Soc.* **89**, 3071 (1967).

⁶) L. F. Fieser and M. J. Haddadin, *Org. Synth.* **46**, 107 (1966).

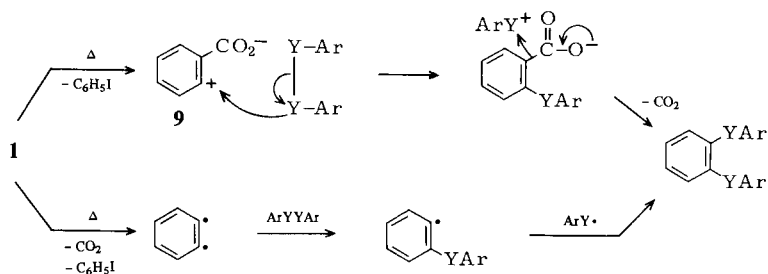
⁷) C. L. Tseng, S. H. Tung, and K. M. Chang, *Sci. Sin.* **13**, 1170 (1964), K'o Hsueh T'ung Pao **1964**, 165 [*Chem. Abstr.* **61**, 7035 h (1964)].

⁸) R. W. Hoffmann in *Dehydrobenzene and Cycloalkynes*, p. 185, Academic Press, New York 1967.

⁹) M. De Moura Campos and N. Petragnani, *Tetrahedron* **18**, 521 (1962).

However, instead of **8**, the products obtained were 2-chlorobenzoic acid (**10**) and the corresponding tellurium oxychloride. Since it is known^{4, 10)} that the thermal decomposition of **1** can involve initial loss of iodobenzene to generate the species **9**, the formation of 2-chlorobenzoic acid can be explained on the basis of the reaction of this species with hydrogen chloride liberated in the hydrolysis of the tellurium chloride by the water of hydration of **1**. In accordance with this mechanism, no **10** was formed when the reaction was carried out with anhydrous iodonium salt **1**.

These results suggested the possibility that, in addition to a mechanism involving concerted insertion of singlet benzyne, the reaction of **1** with ditellurides and diselenides might involve the participation of **9**. Thus, nucleophilic attack of tellurium (or selenium) at the cationic center of **9**, followed by loss of CO₂ and electrophilic attack of the remaining tellurium (or selenium) fragment at the anionic center, would also lead to the observed products.



A third mechanistic possibility, admittedly less probable, would be initial generation of triplet benzyne¹¹⁾ in the decomposition of **1**, followed by homolytic addition across the Te–Te or Se–Se bond.

In order to distinguish between these three mechanistic routes, we examined the reaction of the methyl-substituted iodonium salt **12** with the diaryl selenaditelluride **7**. Reaction *via* the singlet benzyne **13** should result in the formation of a 1:1 mixture of the adducts **14** and **15**. Reaction involving the triplet benzyne **16** should lead to formation of the bis-tellurio and bis-selenio adducts **17** and **18**, respectively, in addition to **14** and **15**. Due to the greater nucleophilicity of tellurium as compared to selenium, reaction *via* the intermediate **11** should exhibit a preference for the formation of **14**.

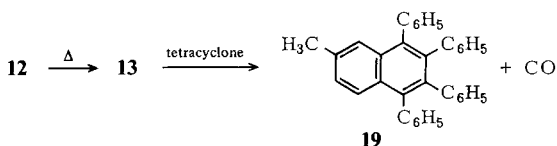
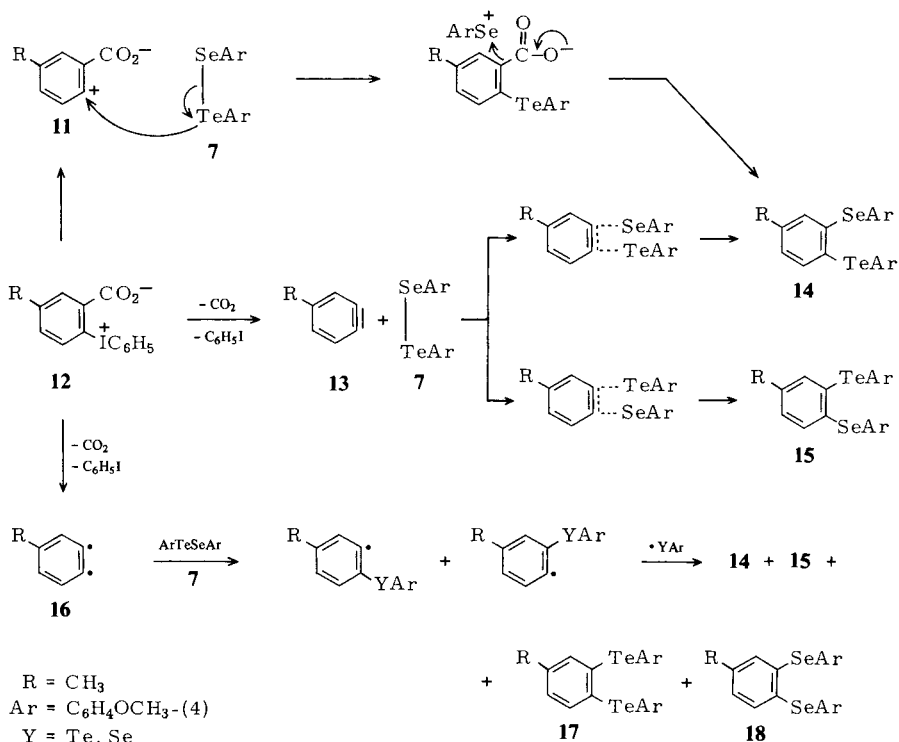
The iodonium salt **12** was prepared in 77% yield by conventional methods⁶⁾. Thermal decomposition of **12** in the presence of tetracyclone yielded the Diels-Alder adduct **19**, supporting the intermediacy of the corresponding benzyne.

The reaction of **12** with bis(4-methoxyphenyl) selenaditelluride (**7**) resulted in a 31% yield of an inseparable 1:1 mixture of **14** and **15** (on the basis of NMR data, see below) which moved as a single spot under TLC conditions. No evidence for the presence of **17** or **18** [which were independently synthesized by reactions of **12** with bis(4-methoxyphenyl) ditelluride or diselenide] in the reaction mixture could be obtained.

These results strongly favor our previously postulated mechanism, i.e. concerted insertion of singlet benzyne into the heteroatom-heteroatom bond.

¹⁰⁾ E. F. Elslager and N. Haley, *J. Heterocycl. Chem.* **9**, 1109 (1972).

¹¹⁾ Reference 8), p. 244.



NMR Spectra

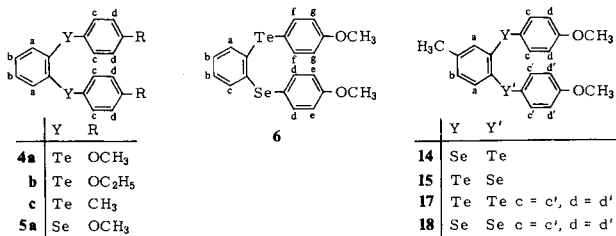
The table summarizes the NMR data of the compounds obtained.

In compounds **17**, **18**, **14**, and **15**, the H_b and H_a protons appear as an ABC type spectrum. The protons H_c and H_d constitute two AA'BB' systems, the one covering a larger chemical shift range corresponding to Te and that with a smaller range corresponding to Se.

Compounds **17** and **18** exhibit two lines for each methoxy group (**17**: $\delta = 3.76, 3.73$; **18**: $3.76, 3.75$). The product obtained in the reaction of **12** with **7** exhibits four lines of equal intensity (in the 100 MHz spectrum) corresponding to the methoxy groups. This result is consistent with a 1:1 mixture of **14** and **15**. The signals of H_c , H_d , H_c' , H_d' of this mixture are superposed, preventing a rigorous attribution.

Nevertheless, the NMR spectrum in this region is in accord with overlapping patterns corresponding to the Se-bonded and Te-bonded phenyl rings.

¹H NMR Chemical shifts (CCl₄, δ, TMS as internal standard, Varian A-60)



| | H _a | H _b | H _c | H _d | OCH ₃ | OCCH ₃ | CH ₃ |
|------------|------------------|------------------|------------------|------------------|------------------|-------------------|-----------------|
| 4b | 7.28–7.06 (m) | 7.00–6.76 (m) | 7.78–7.63 (m) | 6.80–6.65 (m) | 3.98 (q) | 1.30 (t) | |
| 4a | 7.28–7.06 (m) | 7.00–6.76 (m) | 7.80–7.65 (m) | 6.81–6.66 (m) | 3.80 (s) | | |
| 4c* | | 8.56–6.93 (m) | | | | | 2.56 (s) |
| 5a | | 6.96 (s) | 7.55–7.41 (m) | 6.86–6.71 (m) | 3.80 (s) | | |

| | H _a | H _b | H _c | H _d | H _e | H _f | H _g | OCH ₃ |
|----------|----------------|------------------|----------------|------------------|------------------|------------------|------------------|----------------------|
| 6 | 7.36 (s) | 7.36–6.96 (m) | 6.96 (s) | 7.56–7.41 (m) | 6.88–6.73 (m) | 7.86–7.71 (m) | 6.85–6.70 (m) | 3.80 (s) 3.80 (s) |

| | H _a | H _b | H _c | H _d | CH ₃ | OCH ₃ |
|-------------------------------|------------------|------------------|-----------------------------------|-----------------------------------|---------------------------|---------------------------|
| 17 | 7.23–7.00 (m) | 6.95–6.88 (m) | 7.78–7.43 (m) | 6.80–6.63 (m) | 2.11 (s) | 3.76 (s) 3.73 (s) |
| 18 | 7.05–6.86 (m) | 6.86–6.83 (m) | 7.53–7.36 (m) | 6.83–6.68 (m) | 2.15 (s) | 3.76 (s) 3.75 (s) |
| 14/15 (mixture 1:1) | | 7.26–6.86 (m) | c 7.53–7.36(m) c' 7.78–7.43(m) | d 6.83–6.70(m) d' 6.80–6.63(m) | 2.18, 2.14, 2.12, 2.10 | 3.83, 3.81, 3.80, 3.78 |

*¹ Solvent F₃CCO₂H.

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Experimental Part

IR spectra: Perkin-Elmer 337. — ¹H NMR spectra: Varian A 60 and XL 100, tetramethylsilane internal standard. — Melting-points: Thomas Model 40 micro hotstage. — Solvents were dried by standard methods and freshly distilled.

The following compounds were prepared by literature methods: Tellurium tetrachloride¹², bis(4-methoxyphenyl) ditelluride¹³, bis(4-ethoxyphenyl) ditelluride¹³, diphenyl ditelluride¹⁴, di-*p*-tolyl ditelluride¹⁴, di-2-naphthyl ditelluride¹⁵, diphenyl diselenide¹⁶, bis(4-methoxyphenyl)

¹² J. F. Suttle and C. R. F. Smith, *Inorg. Synth.*, vol. III, p. 140, Mc. GrawHill, New York 1950.

¹³ L. Reichel and E. Kirschbaum, *Ber. Dtsch. Chem. Ges.* **76**, 1105 (1943).

¹⁴ W. V. Farrar, *Research (London)* **4**, 177 (1951).

¹⁵ G. Vicentini, E. Giesbrecht, and L. R. M. Pitombo, *Chem. Ber.* **92**, 40 (1959).

¹⁶ K. B. Sharpless and M. W. Young, *J. Org. Chem.* **40**, 947 (1975).

selenaditelluride¹⁷⁾, 2-(phenyliodonio)benzoate (**1**)⁶⁾ (recrystallized from water containing 0.02% EDTA, m.p. 220–222°C). Bis(4-methoxyphenyl) diselenide¹⁸⁾ was prepared by oxidation of 4-methoxyselenophenol¹⁹⁾ with FeCl₃.

2-Iodo-5-methylbenzoic acid: Prepared from 2-amino-5-methylbenzoic acid *via* diazotation and reaction with KI. Yield 74%, m. p. 118–119°C. — IR (KBr): 1672, 1648, 901, 815 cm⁻¹. — ¹H NMR (CF₃CO₂H): δ = 7.98–7.81 (d, 1 H), 7.76–7.33 (m, 1 H), 7.13–6.90 (m, 1 H), 2.36 (s, 3 H).

C₈H₇IO₂ (262.0) Calcd. C 36.65 H 2.67 Found C 36.35 H 2.60

1,2-Bis(4-ethoxyphenyltellurio)benzene (4b): 0.50 g (1 mmol) of bis(4-ethoxyphenyl) ditelluride and 0.65 g (2 mmol) of **1** in 5 ml of 1,2-dichlorobenzene, under argon atmosphere, were heated at 180°C until CO₂ evolution had ceased. The solvent and iodobenzene were removed *in vacuo* and the residue crystallized from glacial acetic acid. Yield 0.37 g (64%), m. p. 114–115°C (in accordance with previous results¹⁾). — IR (KBr): 1248, 1176, 1045, 821, 738 cm⁻¹.

In the same manner, the corresponding ditellurides, diselenides or selenaditelluride were employed to prepare:

1,2-Bis(4-methoxyphenyltellurio)benzene (4a): Yield 53%, m. p. 79–80°C. — IR (KBr): 1248, 1177, 1022, 822, 744 cm⁻¹.

C₂₀H₁₈O₂Te₂ (545.6) Calcd. Te 46.77 Found Te 46.34

1,2-Bis(p-tolyltellurio)benzene (4c): Yield 49.5%, m. p. 82–83°C. — IR (KBr): 1432, 1209, 1066, 796, 777 cm⁻¹.

C₂₀H₁₈Te₂ (513.6) Calcd. Te 49.69 Found Te 49.45

1,2-Bis(4-methoxyphenylselenio)benzene (5a): The crude product was purified by column chromatography (Silica gel 60, Merck 70–230 mesh ASTM, elution with petrol ether 30–50°C), yield 18%. Recrystallized from chloroform/pentane, m. p. 100–101°C. — IR (KBr): 1248, 1170, 1022, 822, 743 cm⁻¹.

C₂₀H₁₈O₂Se₂ (448.3) Calcd. C 53.38 H 4.04 Found C 53.36 H 4.13

1-(4-Methoxyphenylselenio)-2-(4-methoxyphenyltellurio)benzene (6): The crude product was purified by TLC (Silica gel HF 254 Merck, developed with chloroform/petrol ether 30–50°C 1:1). Yield 26%, recrystallized from petrol ether 30–50°C, m. p. 93–95°C. — IR (KBr): 1248, 1175, 1023, 822, 742 cm⁻¹.

C₂₀H₁₈O₂SeTe (496.9) Calcd. C 48.34 H 3.65 Found C 48.20 H 3.72

5-Methyl-2-(phenyliodonio)benzoate (12): Prepared by a procedure similar to that for **1**⁶⁾ starting from 2-iodo-5-methylbenzoic acid. Recrystallized from water containing 0.02 EDTA, m. p. 226–228°C, yield 77%. — IR (KBr): 1632, 1616, 1338, 809 cm⁻¹. — ¹H NMR (CF₃CO₂H): δ = 8.50–8.45 (d, 1 H, J = 2 Hz), 8.25–8.08 (d, 2 H), 8.06–7.90 (d, 1 H, J = 8 Hz), 7.90–7.50 (m, 3 H), 7.06–6.96 (d, 1 H, J = 8 Hz), 3.58 (s, 3 H).

C₁₄H₁₁IO₂ (338.1) Calcd. C 49.72 H 3.27 Found C 49.65 H 3.37

6-Methyl-1,2,3,4-tetraphenylnaphthalene (19): 0.68 g (2 mmol) of 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) and 0.77 g (2 mmol) of **12** in 10 ml of triglyme were heated at 220°C for 1 h under nitrogen atmosphere. The solvent was evaporated *in vacuo*, giving a reddish solid residue. The crude product was purified by column chromatography (Florisil, developed with hexane/

¹⁷⁾ N. Petragnani, L. Torres, and K. J. Wynne, *J. Organomet. Chem.* **92**, 185 (1975).

¹⁸⁾ S. Keimatsu, K. Yokata, and J. Satoda, *J. Pharm. Soc. Jpn.* **53**, 994 (1933) [*Chem. Abstr.* **29**, 3662 (1935)].

¹⁹⁾ L. Chierici and R. Passerini, *Ric. Sci.* **25**, 2316 (1955) [*Chem. Abstr.* **50**, 11 340 (1956)].

carbon tetrachloride 1:1). Yield 0.63 g (75%), m.p. 218–219°C, recrystallized from ethanol, m.p. 221–222°C. — IR (KBr): 1500, 1440, 1070, 1030, 740, 700 cm^{-1} . — ^1H NMR (CCl_4): δ = 7.66–7.26 (m, 3H), 7.16 (s, 10H), 6.16 (s, 10H), 2.40 (s, 3H).

1,2-Bis(4-methoxyphenyltellurio)-4-methylbenzene (17): Prepared from **12** and bis(4-methoxyphenyl) ditelluride (as described for **4**), employing triglyme as solvent, at 210–220°C. The crude product was purified by TLC (Silica gel HF 254 Merck, developed with chloroform/petrol ether 30–50°C 1:1), yield 32%. Recrystallized from petrol ether 30–50°C, m.p. 73–74°C. — IR (KBr): 1504, 1455, 1242, 1174, 1029, 825, 818, 808, 803, 789 cm^{-1} .

$\text{C}_{21}\text{H}_{20}\text{O}_2\text{Te}_2$ (559.6) Calcd. C 45.07 H 3.60 Found C 44.71 H 3.64

1,2-Bis(4-methoxyphenylselenio)-4-methylbenzene (18): Prepared employing diphenyl ether as solvent, at 210–220°C (as described for **4**). The crude product was purified by column chromatography (Silica gel 60, Merck 70–230 mesh ASTM, elution with petrol ether 30–50°C), yield 16%. Recrystallized from chloroform/pentane, m.p. 80–81°C. — IR (KBr): 1488, 1240, 1174, 1018, 825, 818, 811, 788 cm^{-1} .

$\text{C}_{21}\text{H}_{20}\text{O}_2\text{Se}_2$ (462.3) Calcd. C 54.55 H 4.30 Found C 54.52 H 4.53

Mixture of 2-(4-methoxyphenylselenio)-1-(4-methoxyphenyltellurio)-4-methylbenzene (14) and 1-(4-methoxyphenylselenio)-2-(4-methoxyphenyltellurio)-4-methylbenzene (15): A mixture of 0.768 g (2 mmol) of 5-methyl-(2-phenyliodonio)benzoate (**12**) and 0.420 g (1 mmol) of bis(4-methoxyphenyl) selenaditelluride (**7**) in 5 ml of triglyme (freshly distilled from calcium hydride) was heated at 215–225°C (bath temperature) with stirring for one hour under argon atmosphere. Removal of the solvent and iodobenzene *in vacuo* furnished a viscous residue (0.740 g) which was purified by TLC (Silica gel HF 254 Merck, developed with chloroform/petrol ether 30–50°C 1:1). Compounds **17** and **18** (comparison with authentic samples) were not detected. A pure fraction (R_F 0.52, m.p. 96–98°C) was isolated and recrystallized from petrol ether 30–50°C, m.p. 97–98°C, yield 0.160 g (31%). — IR (KBr): 1492, 1243, 1173, 1020, 827, 812, 791 cm^{-1} .

$\text{C}_{21}\text{H}_{20}\text{O}_2\text{TeSe}$ (510.95) Calcd. C 49.36 H 4.18 Found C 49.66 H 4.18

Reaction of 1 with tellurium tetrachloride and aryltellurium trichlorides: 0.27 g (1 mmol) of tellurium tetrachloride and 0.65 g (2 mmol) of **1** in 5 ml of 1,2-dichlorobenzene were heated at 180–190°C for 1 h. After cooling to room temperature, the amorphous precipitate was removed by filtration. This substance (0.21 g), which did not melt below 320°C, exhibits a Te analysis in accordance with TeOCl_2 . The filtrate was evaporated *in vacuo* and the solid residue recrystallized from water, giving 0.30 g of 2-chlorobenzoic acid, m.p. 141–142°C, IR identical to that of an authentic sample.

The analogous reactions with aryltellurium trichlorides (ArTeCl_3 ; $\text{Ar} = 4\text{-CH}_3\text{OC}_6\text{H}_4$, $4\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4$, C_6H_5) furnished the corresponding oxychlorides²⁰⁾ (ArTeOCl , amorphous substances) and 2-chlorobenzoic acid.

Similar experiments employing anhydrous **1** (prepared as described⁶⁾) resulted only in recovery of the starting tellurium halides.

²⁰⁾ N. Petragnani and G. Vicentini, Universidade de São Paulo, Boletim 249-Quimica 5, 1959, 75.