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TELLURIUM IN ORGANIC CHEMISTRY—I

A NOVEL SYNTHESIS OF BIARYLS

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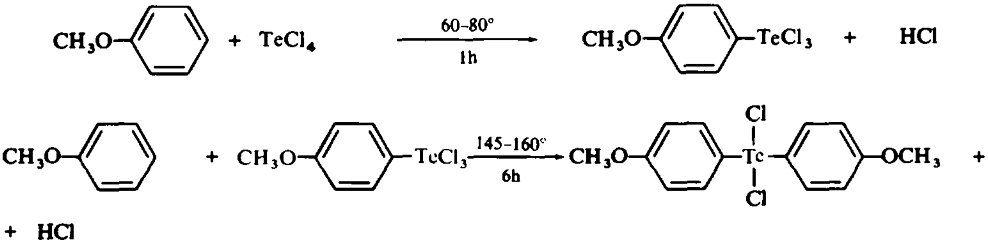
Abstract—Treatment of bis(aryl)tellurium dichlorides or diaryl tellurides with degassed Raney nickel readily affords the corresponding biaryls. The bis(aryl)tellurium dichlorides were prepared from $TeCl_4$ and the appropriate aromatics, with or without a Lewis acid as a catalyst, depending on the reactivity of the aromatic. The diaryl tellurides were prepared by reduction of the dichlorides with hydrazine. Attempts to prepare unsymmetrical dichlorides frequently resulted in exchange reactions ($RTeCl_3 + R'H \rightarrow R'TeCl_3 + RH$).

MOST synthetic methods of biaryls (*e.g.*, the Ullmann coupling and all variants of the Grignard coupling)[1-3] require halogen-substituted aromatics as starting materials. As such components must often be prepared by halogenation of the appropriate aromatic, and not infrequently this has to be done indirectly, it is evident that a direct coupling of the aromatics should be of interest. Such reactions may be effected by $Pd(OAc)_2$,[4-6] $FeCl_3$,[7] $Pb(OAc)_4$[8] and some similar reagents.[7,9] The selectivity is often unsatisfactory, and in the coupling of toluene promoted by $Pd(OAc)_2$ five isomeric dimethylbiphenyls are formed.[6] Furthermore, the yield of the desired product is often reduced by, *e.g.*, acetoxylation. Consequently, trials with new coupling reagents are of interest. In the present paper coupling reactions are studied in which Te-organic reagents were used.

Tellurium tetrachloride reacts as an electrophilic reagent with aromatic compounds bearing activating substituents (*e.g.*, RO—, R_2N—, RS—) giving aryltellurium trichlorides or bis(aryl)tellurium dichlorides,[10] as exemplifed in Scheme 1.

SCHEME 1

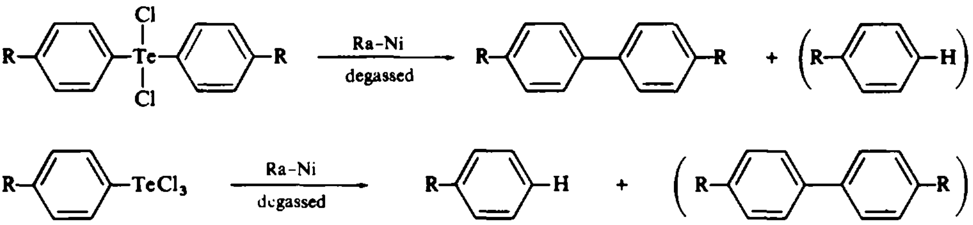


The procedure is very simple, as shown by the following example.

Bis(4-methoxyphenyl)tellurium dichloride. Tellurium tetrachloride (15 g) and anisole (30 g) were heated for 6 hr at 160°, and the solution was then allowed to solidify *in vacuo*. The dichloride, crystallized from acetonitrile, melted at 182–183° (90% yield).

As bis(aryl)tellurium dichlorides are reduced to the corresponding diaryl tellurides by zinc[11] and as diaryl selenides are converted to biaryls on treatment with degassed Raney nickel,[12, 13] it may be expected that bis(aryl)tellurium dichlorides will be reduced and coupled to biaryls in one step by degassed Raney nickel. Aryltellurium trichlorides are considerably less suitable as starting material (Scheme 2).

SCHEME 2



As more than 90% of the working time is required for the laborious preparation of the degassed Raney nickel[14] a modified catalyst, obtained by simply refluxing commercial nickel in 2-methoxyethyl ether or ethylene glycol, has been developed. This catalyst gave, however, somewhat lower and less reproducible yields. The results of the coupling reactions are summarized in Scheme 2 and Table 1.

Attempts to obtain a one-step synthesis by performing the reaction between the aromatic and tellurium tetrachloride in 2-methoxyethyl ether followed by addition of Raney nickel, resulted in a considerably lowered yield, presumably due to complex formation between tellurium tetrachloride and the ether.

Diaryl tellurides, which are likely intermediates in the coupling described above, also gave biaryls in similar yields when treated with Raney nickel. The results are shown in Table 2. In connection with this study it was found that diaryl tellurides as well as diaryl selenides are conveniently prepared by addition of hydrazine to the appropriate dichloride mixed with ethanol. Aryltellurium trichlorides similarly gave diaryl ditellurides.

SCHEME 3

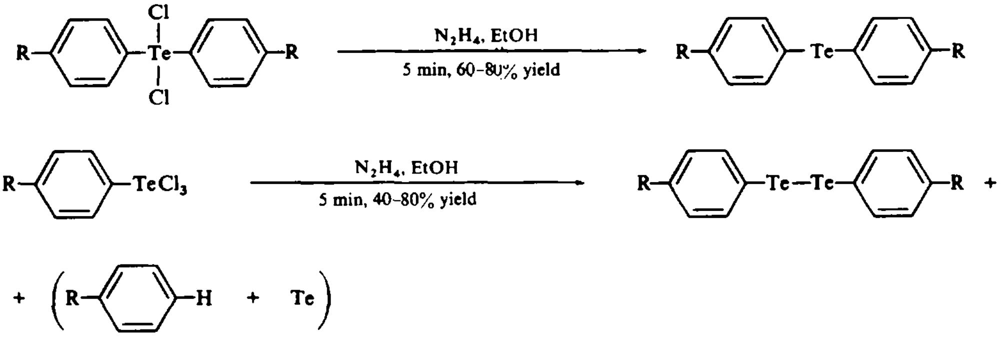


TABLE 1. COUPLING OF BIS-(ARYL)TELLURIUM DICHLORIDES WITH DEGASSED RANEY NICKEL

	Starting material $(R_1R_2Ar)_2\ TeCl_2$[a]	Biaryl	Product			
			Yield, % Procedure A[b]	Yield, % Procedure B[c]	m.p. °C	lit. m.p. °C
1	$R_1 = 4\text{-}OCH_3, R_2 = H$	4,4'-Dimethoxybiphenyl	82	50-70	175-176	176-178[d]
2	$R_1 = 4\text{-}OC_2H_5, R_2 = H$	4,4'-Diethoxybiphenyl	77	50-70	176-177	172-173[e]
3	$R_1 = R_2 = H$	Biphenyl	58	50-60	69-70	70·5[f]
4	$R_1 = 4\text{-}CH_3, R_2 = H$	4,4'-Dimethylbiphenyl	68	50-70	121-122	121-123[g]
5	$R_1 = 4\text{-}Br, R_2 = H$	4,4'-Dibromobiphenyl	60	40-60	162-163	161-163[e]
6	$R_1 = 4\text{-}OCH_3, R_2 = 3\text{-}CH_3$	3,3'-Dimethyl-4,4'-dimethoxybiphenyl	85	60-70	151-152	154·5[h]
7	$R_1 = 4\text{-}OCH_3, R_2 = 3\text{-}OCH_3$	3,3',4,4'-Tetramethoxybiphenyl	91	60-75	132-133	133-134[i]
8	$R_1 = 4\text{-}OCH_3, R_2 = 2\text{-}OCH_3$	2,2',4,4'-Tetramethoxybiphenyl	89	60-75	90-91	90-91[j]
9	$R_1 = 4\text{-}N(CH_3)_2, R_2 = H$	N,N,N',N'-Tetramethylbenzidine	86	50-70	194-195	195-196[d]
10	Bis 2(naphthyl)tellurium dichloride	2,2'-Binaphthyl	83	60-70	183-184	184[d]

[a] Compounds **1-9** are benzene derivatives. The position of the substituents (R_1 and R_2) are given in the table. [b] In procedure A the degassed Raney nickel catalyst was prepared as described in ref. 14. [c] In procedure B a catalyst obtained by refluxing (8 hr) commercial Raney nickel in 2-methoxyethyl ether was used. [d] See ref. 3. [e] G. A. Rasuwajew and M. M. Koton, *Ber. Dtsch. Chem. Ges.* **66**, 1210 (1933). [f] E. Sakellarios and T. Kyrimis, *Ibid.* **57**, 322 (1924). [g] W. Z. Heldt, *J. Org. Chem.* **30**, 3897 (1965). [h] J. van Alphen, *Rec. Trav. Chim.* **50**, 657 (1931). [i] F. H. Howell and D. A. H. Taylor, *J. Chem. Soc.* 4252 (1956). [j] L. Horner and K.-H. Weber, *Chem. Ber.* **96**, 1568 (1963).

TABLE 2. REACTION OF R_2TeCl_2, $RTeCl_3$ AND R_2SeCl_2 WITH N_2H_4 AND SUBSEQUENT COUPLING WITH DEGASSED RANEY NICKEL

Starting material		Product in N_2H_4-reduction step Yield, %	 m.p.(b.p.)°C	 lit. m.p.(b.p.)°C	Product (biaryl) in coupling step Yield, %	 m.p.°C
R_2TeCl_2	R_2Te					
R = 4-Methoxyphenyl	R_2Te	77	55–57	56–57[a]	90[b], 60[c]	175–176
R = Phenyl	R_2Te	78	173–174 (10 mm)	182–183 (16 mm)[d]	81[b]	69–70
R = 4-Methylphenyl	R_2Te	70	69–70	70[e]	89[b]	121–122
R = 4-Ethoxyphenyl	R_2Te	83	63–64	64[f]	72[c]	176–177
R = 4-Bromophenyl	R_2Te	65	115–116	121[g]	79[b]	162–163
$RTeCl_3$	R_2Te_2					
R = 4-Methoxyphenyl	R_2Te_2	68	57–58	60[f]	80[b], 50[c]	175–176
R = Phenyl	R_2Te_2	45	66–67	67[k]	56[b]	69–70
R = 4-Methylphenyl	R_2Te_2	44	51–52	52·5[h]	71[b]	121–122
R = 4-Ethoxyphenyl	R_2Te_2	84	107–108	109[d]	80[c]	176–177
R = 4-Bromophenyl	R_2Te_2	48	153–154	153–155[i]	63[b]	162–163
R = 3-Methyl-4-methoxyphenyl	R_2Te_2	57	77–78	78[f]	59[c]	151–152
R_2SeCl_2	R_2Se					
R = Phenyl	R_2Se	75	156–158 (10 mm)	165–167 (12 mm)[j]	80[b], 54[c]	69–70
R = 4-Methoxyphenyl[k]	R_2Se	88	57–58	56·5–58[l]	84[b], 45[c]	175–176

[a] See ref. 26. [b] Procedure A was used. [c] Procedure B was used. [d] L. Reichel and E. Kirschbaum, *Ber. Dtsch. Chem. Ges.* **76**, 1105 (1943). [e] K. Lederer, *Ibid.* **48**, 2049 (1915). [f] See ref. 11. [g] See ref. 20. [h] See ref. 27. [i] See ref. 18. [j] A. Schoeller, *Ber. Dtsch. Chem. Ges.* **52**, 1517 (1919). [k] F. N. Alquist and R. E. Nelson, *J. Am. Chem. Soc.* **53**, 4033 (1931). [l] G. V. Boyd, M. Doughty and J. Kenyon, *J. Chem. Soc.* 2196 (1949).

The preparation of bis(aryl)tellurium dichloride by the simple procedure exemplified in Scheme 1, is unfortunately restricted to activated aromatics. Less reactive aromatics, such as toluene and benzene, require higher reaction temperatures (135–150° to obtain trichlorides). Bromobenzene, but not chlorobenzene, gave the trichloride, when boiled (12 h) with tellurium tetrachloride. When treated similarly, benzonitrile gave, not unexpectedly,[15] 2,4,6-triphenyl-*sym*-triazine, while ethyl benzoate gave an unidentified crystalline product.

By addition of Lewis acids to the reactants the reaction temperature could be lowered. Thus, benzene reacted at 80° to give a mixture of trichloride and dichloride as shown below (R = H).

$$C_6H_5R \xrightarrow[\text{Lewis acid}]{TeCl_4} RC_6H_4TeCl_3 + RC_6H_4TeCl_2C_6H_4R$$

Similar results were obtained with toluene, chlorobenzene and bromobenzene. The required dichloride was always accompanied by the trichloride, even with strong catalysts ($AlCl_3$) and long reaction times (reflux 24 hr). Most of the trichloride was removed by filtration. The presence of a small amount (~10%) of trichloride had only a slight influence on the biaryl yield in the subsequent detelluration.

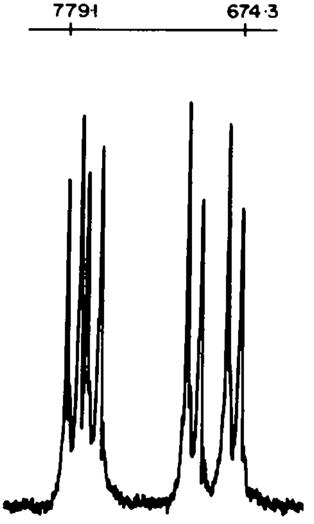
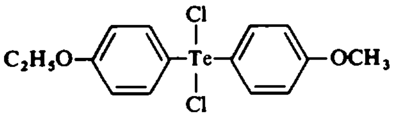


Fig. 1a. NMR spectrum (100 MHz) of 4-ethoxyphenyl-4-dimethylaminophenyltellurium dichloride (12)

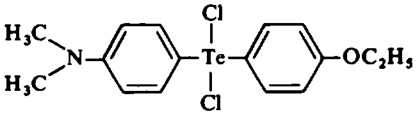
Fig. 1b. NMR spectrum (60 MHz) of bis(4-dimethylaminophenyl) tellurium dichloride (9)

In this connection it should be noted that diaryltellurium dichlorides may also be prepared *via* Hg-, Mg- or Li-organic reagents[16–19] as well as diazonium salts.[20–21] The total yield in the complicated and incompletely studied reactions are not always satisfactory.

The formation of a diaryltellurium dichloride generally proceeds in two distinct steps (*cf* Scheme 1). Hence, the preparation of an unsymmetrical dichloride should be simple.



11

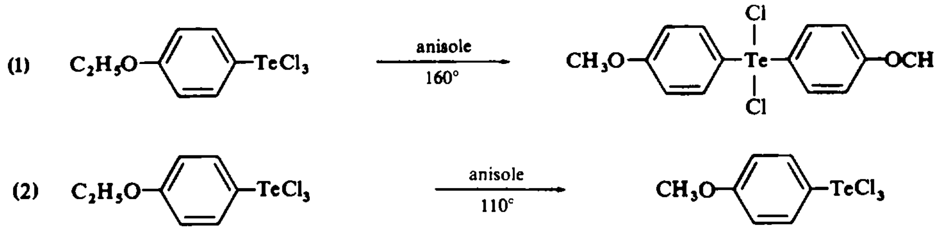


12

A few compounds (*e.g.*, **11** and **12**) prepared by this procedure are reported in the literature.[11,20] Attempts to reproduce **11** by heating 4-ethoxyphenyl tellurium trichloride (1 mol) with anisole (4 mol) at 160° for 6 hr as described in the literature[11] were unsuccessful. The symmetrical compound, bis(4-methoxyphenyl)tellurium dichloride was always isolated as indicated by reaction (1) in Scheme 4.

The reaction between N,N-dimethylaniline and 4-ethoxyphenyltellurium trichloride, which can be performed at considerably lower temperatures (25–35°), gave the unsymmetrical product **12** as described by Petragnani.[22] At higher temperatures complicated reactions occurred. The NMR-signals from the aromatic protons of compound **12** are given in Fig. 1a.

SCHEME 4



From Scheme 4 it is apparent that exchange of the $TeCl_3$-substituent may be a common process. Further studies showed that other aryltellurium trichlorides, such as $4\text{-}BrC_6H_4TeCl_3$ and $4\text{-}CH_3C_6H_4TeCl_3$ also transferred the $TeCl_3$-group to anisole under the given conditions.

As yet no attempts have been made to determine equilibrium constants or to elucidate reaction mechanisms. Other interesting experiments that should be made, include equilibration studies of unsymmetrical diaryl dihalotellurides.

EXPERIMENTAL

M.ps were determined on a microhot stage and are uncorrected. The NMR spectra were determined with a Varian A60-A instrument (unless stated otherwise) using DMSO-d_6 as solvent and with TMS as internal standard.

*Chemicals.*Tellurium tetrachloride (BDH) and Raney nickel "gebrauchfertig" (FLUKA) were used as obtained.

Bis(4-methoxyphenyl)tellurium dichloride (1). $TeCl_4$ (27·0 g, 0·1 mol) and anisole (64·8 g, 0·6 mol) were heated for 6 hr at 160°, the soln was then allowed to solidify *in vacuo*. The dichloride crystallized from acetonitrile (with final cooling to − 15°) melted at 182–183° (90% yield) (lit.[23] 181–182°, 95%). NMR: (τ) 6·19 (s, 6, OCH_3): 2·92 (d, 4, 3-H and 5-H, $J = 9$ Hz): 2·07 (d, 4, 2-H and 6-H, $J = 9$ Hz).

The following compounds were similarly prepared

Bis(3,4-dimethoxyphenyl)tellurium dichloride (**7**). Yield: 65%, m.p. 155–156°. (Found: C, 40·8: H, 3·9: Cl, 14·5: Te, 25·9. Calc. for $C_{16}H_{18}Cl_2O_4Te$: C, 40·8; H, 3·8: Cl, 15·0: Te, 27·0%): NMR: (τ) 6·16 (s, 3, OCH_3): 6·11 (s, 3, OCH_3): 2·83 (d, 2, 5-H, $J_{5-6} = 9$ Hz): 2·41–2·25 (3d, 4, 2-H and 6-H, $J_{2-6} = 2·5$ Hz). *Bis(2,4-dimethoxyphenyl)tellurium dichloride* (**8**). Yield: 63%, m.p. 203–204° (lit.[24] 204–205°). *Bis(4-ethoxyphenyl)tellurium dichloride* (**2**). Yield: 88%, m.p. 106–107° (lit.[11] 108). *Bis(3-methyl-4-methoxyphenyl)tellurium dichloride* (**6**). The procedure used for **1** above failed, presumably due to the insolubility and high m.p. of the intermediate trichloride. The required compound could be prepared, however, by the following modified procedure:

$TeCl_4$ (27·0 g), 2-methylanisole (24·4 g, 0·2 mol) and 2-methoxyethyl ether (80 ml) were refluxed for 6 hr, whereupon the solvent was removed *in vacuo*. The dichloride crystallized from EtOH (with final cooling to − 15°) melted at 146–147° (52% yield). (Found: C, 43·3: H, 4·0: Cl, 16·2: Te, 29·6. Calc. for $C_{16}H_{18}Cl_2O_2Te$: C, 43·6: H, 4·1: Cl, 16·1: Te, 29·0%): NMR: (τ) 7·82 (s, 3, CH_3): 6·15 (s, 3, OCH_3): $J_{5-6} = 9$ Hz, $J_{2-6} = 2·5$ Hz.

4-Bromophenyltellurium trichloride. $TeCl_4$ (27·0 g, 0·1 mol) and bromobenzene (150 ml) were refluxed for 12 hr. The mixture was allowed to cool and the crystals formed were collected, washed with benzene and dried in a vacuum desiccator, Yield: 38%, m.p. 210° d. (Found: C, 18·2: H, 0·93: Cl, 26·4: Te, 33·5. Calc. for $C_6H_4BrCl_3Te$: C, 18·5: H, 1·04: Cl, 27·3: Te, 32·8%).

Bis(4-methylphenyl)tellurium dichloride (**4**). $TeCl_4$ (27·0 g, 0·1 mol) was refluxed with toluene (150 ml) for 0·5 hr, whereupon the soln was cooled to 60°, and $AlCl_3$ (1·0 g) was added. Evolution of HCl ensued. The mixture was then refluxed for 12 hr, allowed to cool, filtered to remove the trichloride and the inorganic impurities formed. After evaporation, the residue was crystallized from CH_3CN, yield: 42%, m.p. 164–165° (lit.[20, 25] 163·5–164, 166–167°).

The following compounds were similarly prepared

Bis(phenyl)tellurium dichloride (**3**). Yield: 36%, m.p. 160–161° (lit.[20] 159–160°). *Bis(4-bromophenyl)tellurium dichloride* (**5**). Yield: 44%, m.p. 190–191° (lit.[20] 190°). *Bis(4-chlorophenyl)tellurium dichloride*. Yield: 31%, m.p. 182–183° (lit.[20] 182–183°).

Coupling experiments

Procedure A. Bis(aryl)tellurium dichloride (0·05 mol) was heated with degassed[14] Raney nickel (60 g) in 2-methoxyethyl ether (500 ml) for 8 hr. The mixture was filtered while still hot and the solvent evaporated. The residue was recrystallized from ethanol or toluene. The results are given in Table 1.

Procedure B. Commercial Raney nickel (60 g) in 2-methoxyethyl ether (500 ml) was refluxed for 8 hr. The bis(aryl)tellurium dichloride (0·05 mol) in 2-methoxyethyl ether (100 ml) was then added and the reflux continued for 8 hr. The mixture was then worked up as described in procedure A. The results are given in Table 1.

Coupling of diaryl tellurides, diaryl ditellurides and diaryl selenides. Procedure A or B was used without alterations. The results are given in Table 2.

Bis(4-methoxyphenyl) telluride.

Hydrazine (3·2 g, 0·1 mol) in EtOH (20 ml) was added slowly to a refluxing mixture of bis(4-methoxyphenyl)tellurium dichloride (8·3 g, 0·02 mol) and EtOH (150 ml) and water (15 ml). In the beginning every addition resulted in vigorous evolution of N_2 and the dichloride dissolved gradually. The reaction was considered completed when an addition of hydrazine no longer caused evolution of N_2. The mixture was poured into water (700 ml) and extracted with ether (2 × 300 ml). After washing (H_2O), drying and evaporation, the residue was recrystallized from MeOH with final cooling to − 25°, yield: 5·2 (77%), m.p. 55–57° (lit.[26] 56–57°): NMR: (τ) 6·29 (s, 6, OCH_3): 3·23 (d, 4, 3-H and 5-H, $J = 9$ Hz): 2·34 (d, 4, 2-H and 6-H, $J = 9$ Hz).

Other tellurides prepared by this procedure are given in Table 2.

Bis(4-methylphenyl) ditelluride.

4-Methylphenyltellurium trichloride (3·25 g, 0·01 mol) in EtOH was treated with hydrazine as described above. When the evolution of N_2 had ceased, the mixture was filtered while still hot. On cooling (finally to − 25°) orange crystals separated, yield: 0·95 g (44%), m.p. 51–52° (lit.[27] 52·5); NMR: (τ) 7·66 (s, 6, CH_3): 3·10 (d, 4, 3-H and 5-H, $J = 9$ Hz); 2·35 (d, 4, 2-H and 6-H, $J = 9$ Hz).

Other ditellurides prepared by this procedure are given in Table 2.

2,4,6-Triphenyl-sym-*triazine*

A mixture of tellurium tetrachloride (27·0 g, 0·1 mol) and benzonitrile (103·3 g, 1 mol)) was heated (190°) for 12 hr and then, while still hot, poured into toluene (1·2 l). The crystals (95 g) formed were collected, and a sample was recrystallized from toluene for analysis.

This material (m.p. 232–234°) agreed completely (IR and mixed m.p.) with a sample prepared as described by Cook and Jones.[28]

Exchange reactions

4-Ethoxyphenyltellurium trichloride and anisole at 160°. 4-Ethoxyphenyltellurium trichloride (3·39 g, 0·01 mol) was heated with anisole (5·4 g, 0·05 mol) at 160° for 6 hr, and the soln allowed to solidify *in vacuo*. The residue recrystallized from CH_3CN or HOAc gave bis(4-methoxyphenyl)tellurium dichloride (yield 80%, m.p. 182–183°).

Exchange reactions between anisole and 4-bromophenyltellurium trichloride and 4-methylphenyltellurium trichloride respectively also gave bis(4-methoxyphenyl)tellurium dichloride.

4-Ethoxyphenyl-4-dimethylaminophenyltellurium dichloride (**12**). 4-Ethoxyphenyltellurium trichloride (10·2 g, 0·03 mol) was added in ten portions to N,N-dimethylaniline (12·1 g, 0·1 mol) at 25°. Thereafter the mixture was kept at 25° for 6 hr. MeOH (40 ml) was added and the crystals formed were separated after 1 hr. Recrystallization from EtOH or CH_3CN gave yellow crystals, 7·0 g (53%), m.p. 154–156° (lit.[22] 153–154°); NMR: (τ) 8·63 (t, 3, $CH_2\underline{CH_3}$); 6·99 (s, 6, $N(CH_3)_2$); 5·87 (q, 2, $\underline{CH_2}CH_3$). The signals from the aromatic protons are shown in Fig. 1a.

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