Reaction of 1,1-Diarylethylenes with Tellurium Halides

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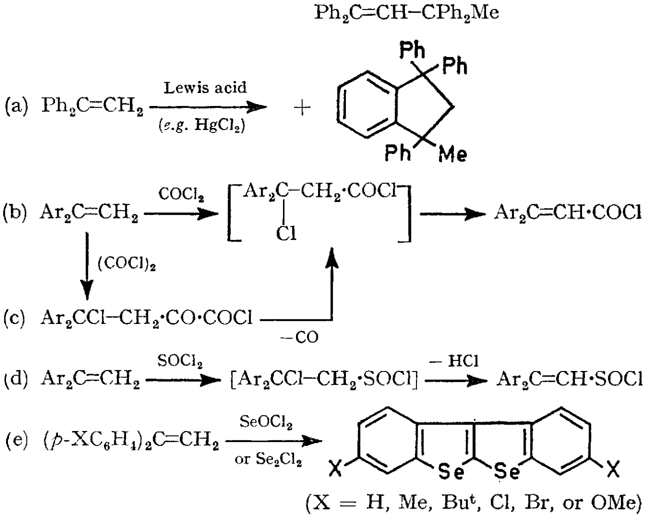
The reaction of 1,1-diarylethylenes with tellurium tetrachloride gives dimers as well as adducts containing two molecules of the ethylenes bound to $TeCl_2$. The u.v., i.r., n.m.r., and mass spectra of the adducts have been measured and the influence of temperature and solvent changes on the n.m.r. spectra has been studied. Several possible structures are proposed and discussed. The chlorine atoms in the adduct $(Ph_2C{=}CH_2)_2TeCl_2$ (IIa) can be exchanged for other halogen atoms. Various reactions of the adducts have been studied, in some of which the tellurium atom is retained in a σ-bonded bis-(2,2-diarylvinyl) telluride product while in others it is lost, yielding products derived from the 1,1-diarylethylene portion only.

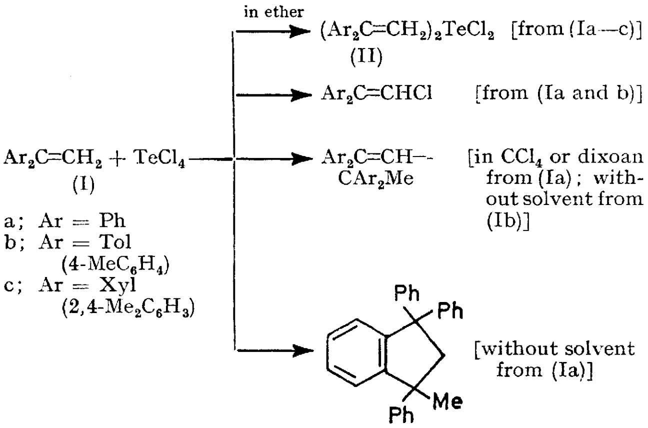
WE have previously studied the reactions of 1,1-diarylethylenes with various halides and oxyhalides.[1-5] Some of the products obtained were those expected from the reactions of protonic or Lewis acids with the ethylenes, *i.e.* linear and cyclic dimers [2,4,6] [route (a)], whereas phosgene (b; Ar = p-MeO·C_6H_4),[1] oxalyl chloride [1,7] (c), and thionyl chloride [3] (d) yielded products derived from 1,2-addition to the double bond. The reactions of seleninyl chloride [5] or diselenium dichloride [8] with the same ethylenes yielded tetracyclic aromatic compounds containing two selenium atoms in two adjacent condensed five-membered aromatic rings (e).



Tellurium tetrachloride is known to catalyse polymerization [9a] as well as to add to ethylenic double bonds.[9b,c] With 1,1-diarylethylenes it was expected to react through one or more routes similar to (a)—(c). In fact, in addition to dimers and dehydrodimers of the 1,1-diarylethylenes, tellurium tetrachloride produced completely different adducts, composed of two molecules of the diarylethylenes and one of tellurium dichloride.

RESULTS

The products obtained from 1,1-diarylethylenes (I) and tellurium tetrachloride are summarized in Scheme 1.



SCHEME 1

The products (II) were obtained in rather low yields (10% with Ph, 19% with Tol, 36% with Xyl). All other products are known from previous work. The amount of (II) and of the dimers obtained was markedly dependent on the conditions, particularly on the solvent used. A number of methyl- and methoxy-substituted 1,1-diarylethylenes yielded only intractable tars and no products at all were obtained with stilbene or diphenylmethane.

No product could be obtained from tellurium dichloride or dibromide with (Ia) except the linear dimer $Ph_2C{=}CH{-}CPh_2Me$, in low yield. Tellurium tetrabromide gave no adducts; with (Ia) it yielded the head-to-tail dimer, and with (Ib) the product of a head-to-head dimerization with dehydrogenation; (Ic) was recovered unchanged.

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[1] F. Bergmann, M. Weizmann, E. Dimant, S. Patai, and J. Szmuskowicz, *J. Amer. Chem. Soc.*, 1948, **70**, 1612.

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[8] D. Elmaleh, unpublished experiments.

[9] C. H. Fischer and A. Eismer, *J. Org. Chem.*, 1941, **6**, 169; (*b*) H. Funk and W. Weiss, *J. prakt. Chem.*, 1954, **1**, 33; (*c*) H. J. Arpe and H. Kuckertz, *Angew. Chem.*, 1971, **83**, 81; M. Ogawa, *Bull. Chem. Soc., Japan*, 1968, **41**, 3031; M. Ogawa and R. Ishioka, *ibid.*, 1970, **43**, 496.

$$2Ph_2C{=}CH_2 \xrightarrow{TeBr_4} Ph_2C{=}CH{-}CPh_2Me \qquad (57\%)$$

$$2Tol_2C{=}CH_2 \xrightarrow{TeBr_4} Tol_2C{=}CH{-}CH{=}CTol_2 \qquad (38\%)$$

The reaction of tellurium tetrachloride with 1,1-diphenylpropene gave 2-methyl-1,1,3,3-tetraphenylpropene,[10] probably obtained by the elimination of the elements of C_2H_4 from a head-to-tail dimer, possibly involving Lewis-acid catalysis by tellurium tetrachloride. Although reported [9a] to yield

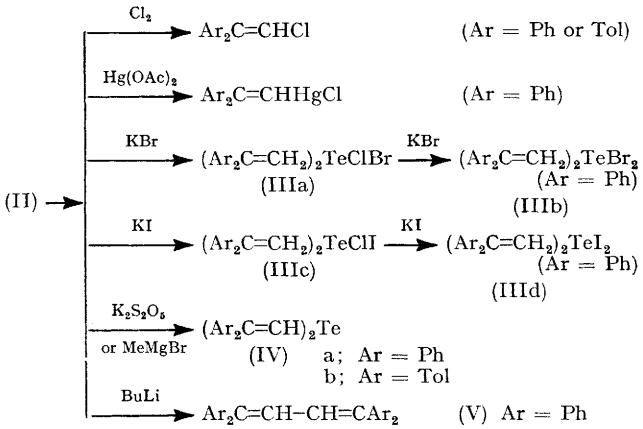
$$Ph_2C{=}CHMe \xrightarrow{TeCl_4} Ph_2C{=}CMe{-}CHPh_2$$

a polymer, under our conditions styrene and tellurium tetrachloride gave a product whose molecule apparently contained a $C_{16}H_{14}$ entity (probably a dehydrodimer, since the base peak of its mass spectrum is at *m*/*e* 206), and three atoms of chlorine. This compound was not investigated further.

Apparently, the formation of $(Ar_2C{=}CH_2)_2TeCl_2$ (II) is confined to a relatively small number of 1,1-diarylethylenes (Ia—c) and the use of styrene or of $Ph_2C{=}CHMe$ directs the product formation into different pathways.

Reactions of the Adducts (II) (*Scheme* 2).—(a) *Electrophilic reagents.* These yield products derived from the parent diarylethylene. Thus chlorine with (IIa or b) gives the corresponding 1,1-diarylvinyl chloride and tellurium tetrachloride, while mercury(II) acetate with (IIa) yields 1,1-diphenylvinylmercury(II) chloride, probably through substitution of the primarily formed 1,1-diphenylvinylmercury(II) acetate by halide ions.

(b) *Halide exchange.* One or both of the chlorine atoms in (IIa) could be exchanged for other halogen atoms. In this manner, compounds (IIIa—d) were prepared in *ca.* 70% yields.



SCHEME 2

(c) *Internal elimination.* Dehydrochlorination of (IIa and b) could be carried out with good yields either by potassium disulphite [11] or by methylmagnesium bromide (which was expected to exchange the chlorine atoms for Me groups). The spectra (u.v., i.r., and n.m.r.) and elemental analyses of the products agree with the assumption that these are covalently bound tellurides, *i.e.* bis-(2,2-diphenylvinyl) telluride (IVa), and bis-(2,2-di-*p*-tolylvinyl) telluride (IVb).

Attempted alkylation of (IIa) by butyl-lithium gave the head-to-head dehydrodimer (V).

Stability and Properties of the Adducts.—Exchange of one ligand for another in adducts often takes place readily. This was not so in the present case; treatment of (IIa) with excess of 1,1-di-(*p*-tolyl)ethylene (Ib) did not give a new product.

Most of (IIa) was recovered unchanged (m.p., n.m.r., and analysis) after refluxing for prolonged periods in aqueous acetone, carbon tetrachloride, chlorobenzene, or triethylamine.

The solid adducts, on exposure to sunlight turned red after a few min and black after several h, probably as a result of the separation of metallic tellurium. Solutions only turned red, with the precipitation of traces of metallic tellurium, after several h. Solutions (about 0·003M) of (IIa) in acetone–water (80 : 20 v/v), dimethyl sulphoxide, and dimethylformamide at 25° had equivalent conductivities of 33·6, 2·0, and 3·3 Ω^{-1} cm^{-1} M^{-1}, respectively. On addition of an aqueous solution of silver nitrate to an acetone solution of (IIa), silver chloride precipitated immediately indicating that chloride ions are present in solutions of (IIa).

U.v. and I.r. Spectra.—The main features of the u.v. spectra of the 1,1-diarylethylenes, their adducts with TeXY (X or Y = Cl, Br, or I), and some products obtained from the adducts are given in Table 1.

TABLE 1

U.v. spectral data

Compound	$\lambda_{max.}$/nm ($CHCl_3$)	ε	$\lambda_{max.}$/nm (MeCN)	ε
$Ph_2C{=}CH_2$ (Ia)			231	14,200
$(Ph_2C{=}CH_2)_2TeCl_2$ (IIa)	303	21,800	297	21,200
$(Ph_2C{=}CH_2)_2TeBr_2$ (IIIb)	313	14,600		
$(Ph_2C{=}CH_2)_2TeI_2$ (IIId)	360	15,500	352	17,800
$(Ph_2C{=}CH_2)_2TeClBr$ (IIIa)	309	15,200	305	17,700
$(Ph_2C{=}CH_2)_2TeClI$ (IIIc)	323	16,800		
$(Ph_2C{=}CH)_2Te$ (IVa)	344	17,100	340	20,300
$Tol_2C{=}CH_2$ (Ib)			236·5	20,100
$(Tol_2C{=}CH_2)_2TeCl_2$ (IIb)	311	23,000	304	21,500
$(Tol_2C{=}CH)_2Te$ (IVb)	258	22,000	256	24,000
	356	32,000	350	34,000
$Xyl_2C{=}CH_2$ (Ic)			237	18,600
$(Xyl_2C{=}CH_2)_2TeCl_2$ (IIc)	305	19,000	293	19,000

Compared to the parent diarylethylenes, the adduct maximum absorptions are shifted to higher wavelengths. In the series X = Cl, Br, I, in $(Ph_2C{=}CH_2)_2TeX_2$, a bathochromic shift is observed, most of the shift occurring between X = Br and I, and similarly in the series $(Ph_2C{=}CH_2)_2TeClX$, the shift is larger between ClBr and ClI. The maxima are at shorter wavelengths than those observed for tellurium dibromide [$\lambda_{max.}$ (ether) 473, 383, 316, and 228 nm] and for tellurium di-iodide [$\lambda_{max.}$ (ether) 510, 390, and 310 nm].[12]

I.r. spectra (KBr). The most important bands are given in Table 2. It seems that the C=C stretching bands in the tellurium derivatives are shifted to lower wave-numbers compared with (Ia and b).

Mass Spectra.—Of the many isotopes of tellurium six have a natural abundance >2% and must be considered in the mass spectra of tellurium compounds.[13a] These

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[10] C. F. Koelsch and R. V. White, *J. Amer. Chem. Soc.*, 1943, **65**, 1639.

[11] R. Samuel and M. Usman, *Proc. Indian Acad. Sci.*, 1937, **5***A*, 425.

[12] C. Courtot and M. G. Bastani, *Compt. rend.*, 1936, **203**, 197.

[13] Robert Weast, ed. ' Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland, Ohio, 50th edn. (1969—70), (*a*) pp. B356—B3561; (*b*) p. B274.

have masses 122 (2·46%), 124 (4·61%), 125 (6·99%), 126 (18·71%), 128 (31·79%), and 130 (34·48%).

Each fragment RTe^+ will show six signals with the above distribution, spaced over nine mass units. In fragments also containing chlorine, the two isotopes of the latter [13b] will contribute to the multiplicity of the signals. Choosing as the base M' a fragment containing ^{35}Cl and ^{122}Te, the following distribution is expected, with the relative abundance in parentheses: M' (1·8), $M' + 2$ (3·9), $M' + 3$ (5·3), $M' + 4$ (15·1), $M' + 5$ (1·7), $M' + 6$ (28·7), $M' + 8$ (35·8), and $M' + 10$ (8·6).

TABLE 2

I.r. spectra of starting materials and products

Compound	ν(C–H)/cm⁻¹	Other absorptions (cm⁻¹)
$Ph_2C{=}CH_2$ (Ia)	3025m, 3055m, 3075m, 2920vw	1655w, 1605m, 1575m, 1500m, 1445s
$(Ph_2C{=}CH_2)_2TeCl_2$ (IIa)	3070m, 3040m, 3020m, 2920m, 2860w	1605w, 1510s, 1450vw, 825vs
$(Ph_2C{=}CH_2)_2TeBr_2$ (IIIb)	3050m, 3020m, 2920w	1620w, 1580w, 1550m, 1490m, 1440s, 710s
$(Ph_2C{=}CH_2)_2TeI_2$ (IIId)	3050m, 3030m, 3010m, 2920m, 2850w	1615m,br, 1550m, 1490m, 1442s, 705vs
$Tol_2C{=}CH_2$ (Ib)	3060w, 3040w, 3020w, 2920w, 2850w	1650m, 1600m, 1560w, 1500s, 1400m, 825vs
$(Tol_2C{=}CH_2)_2TeCl_2$ (IIb)	3010m, 2905m, 2850m	1600s, 1575m, 1540m, 1500s, 1440m, 825vs
$(Ph_2C{=}CH)_2Te$ (IVa)	3050m, 3010m	1600m, 1590m, 1490s, 1440s
$(Tol_2C{=}CH)_2Te$ (IVb)	3020m, 2920m, 2850w	1600m, 1550m, 1500s, 1450m, 1400m, 830s

For a fragment M (such as the molecular ion) containing two atoms of ^{35}Cl one of ^{122}Te the following distribution is expected: M (1·7), $M + 2$ (3·5), $M + 3$ (4·3), $M + 4$ (12·5), $M + 5$ (2·7), $M + 6$ (25·3), $M + 8$ (32·6), $M + 10$ (14·9), and $M + 12$ (2·2). In (IIa and b) the molecular peaks are weak and show only the largest abundances. (IIc) shows clearly the ratios 11·5 : 23 : 35 : 15 at m/e 668 ($M + 4$), 670 ($M + 6$), 672 ($M + 8$), and 674 ($M + 10$), respectively, in reasonable agreement with calculated values.

The (M – Cl) peak in (IIa—c) shows the five most intense lines with abundance ratios fitting reasonably well the expected values; *e.g.*, for (IIb) the observed lines are 576 [($M' + 3$) 5·5%], 577 [($M' + 4$) 15·2%], 579 [($M' + 6$) 33·1%]; 581 [($M' + 8$) 38·6%], and 583 [($M' + 10$) 7·6%].

The chlorine-free fragments usually show the main lines attributable to the four or five most abundant isotopes of tellurium. In the high-molecular weight region of (IIb) (relative abundances in parentheses) lines appear at m/e 540 (3·5), 541 (8·34), 542 (23·3), 544 (39·2), and 546 (44·1). These are in good agreement with the expected tellurium isotope-determined abundances of a $M - 2Cl$ fragment, which can be rationalized as $(Tol_2C{=}CH_2)_2Te^+$.

Figure 1 shows the mass spectrum of the dichloride (IIa). The base peak, m/e 179, corresponds to a diphenylvinyl ion. The second largest peak, m/e 214, corresponds to diphenylvinyl chloride (verified by the appearance of a line at m/e 216, with one third of the intensity, as expected from the 3 : 1 abundance of the two chlorine isotopes). The third largest peak is at 180, compatible with a diphenylethylene unit. Other fragments correspond to the loss of one or two hydrogen chloride molecules and/or the loss of a diphenylethylene unit. M^+, $(M - Cl)^+$, and $(M - Cl_2)^+$ peaks are rather weak.

The base peak of (IIb) is at m/e 242, again with a $P + 2$ peak of one-third intensity (probably $Tol_2C{=}CHCl)^+$. The second largest peak is at m/e 192 corresponding to the loss of CH_4 (or CH_3 and H) from (Ib). Other fragments correspond to similar processes as with (IIa).

In the spectrum of (IIc) fragments due to CH_3 or CH_4 loss become abundant. In this case the $(M - Cl_2)^+$ peak becomes the base peak at m/e 602 (for ^{130}Te). This peak is small (2%) in (IIa), larger in (IIb) (44%) and is dominant in (IIc). Fragments compatible with tetra-arylbutadienes appear in the spectra of all three compounds.

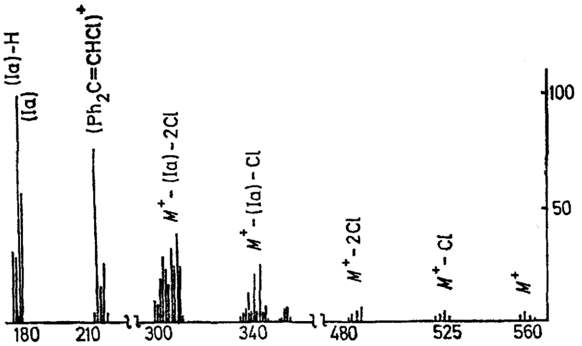

FIGURE 1 Mass spectrum of tellurium dichloride–bis-(1,1-diphenylethylene (IIa)

Bis-(2,2-diphenylvinyl) telluride showed the six tellurium isotopes in the molecular ion peak (total relative abundance 50%). The base peak was at m/e 178, corresponding to a Ph_2C_2 unit. The second largest peak was at m/e 179 $(Ph_2C{=}CH)^+$. These two signals probably result from processes analogous to those forming the m/e 179 and 180 peaks from (IIa). Peaks at m/e 358 (12%) and 357 (35%) correspond to $(M - Te)^+$ and $(M - Te - H)^+$.

The mass spectra of (IIIa—d) each showed signals at 180 and 179 ($Ph_2C{=}CH_2$ and $Ph_2C{=}CH$) and also at 490 (M – 2Hal) and 360 (dimer of $Ph_2C{=}CH_2$). With (IIIa and c) the peak corresponding to $Ph_2C{=}CHY$ was observed (Y = Br or I), while the $Ph_2C{=}CHCl$ peak was small or absent.

The mass spectra show unequivocally that the molecular weights of compounds (II) and (III) agree with the proposed composition.

Comparison of the mass spectra of (IIa—c) suggests that methylation of the aryl group increases the stability of the diarylethylene–tellurium bond relative to the tellurium–chlorine bond. This is shown by the preferential loss of chlorine to give relatively more abundant $M{-}Cl_2$ fragments in the series Ph < Tol < Xyl, despite the increased possibilities of methyl loss in the more methylated compounds.

The fragments corresponding to diarylvinyl halides, diarylethylene dimers, and tetra-arylbutadienes can be formed by fragmentation–recombination processes either in the ionization chamber or thermally in the heating zone.

The fact that the same compounds are also obtained in the synthetic procedure (Schemes 1 and 2) may support the second possibility.

N.m.r. Spectra.—The adducts, compared to the parent diarylethylenes (Ia—c), show a pronounced downfield shift (1·8—2·6 p.p.m.) in the vinyl proton signals, which appear as two peaks of equal intensity (Table 3). A much smaller downfield shift is observed in methyl signals when present, as well as in the aromatic peaks, but the latter show again two signals of equal intensity about 0·1 p.p.m. apart (see Figure 2). All integrations were compatible with the data given in Table 3. The superscripts used throughout are 1 for the lower field and 2 for the higher field protons.

TABLE 3

Chemical shifts (δ in p.p.m. downfield from Me_4Si) for tellurium adducts and parent 1,1-diarylethylenes in CCl_4 at 35 °C (100 MHz)

Compound	δ(H¹)		δ(H²)	δ(Ar¹)		δ(Ar²)
$Ph_2C{=}CH_2$ (Ia)		5·39			7·26	
$Tol_2C{=}CH_2$ [a] (Ib)		5·25			6·98	
$Xyl_2C{=}CH_2$ [b] (Ic)		5·32			6·80—7·15 [b]	
$(Ph_2C{=}CH_2)_2TeCl_2$ (IIa)	7·91		7·22	7·43		7·33
$(Tol_2C{=}CH_2)_2TeCl_2$ [c] (IIb)	7·81		[i]		7·00—7·38 [c]	
$(Xyl_2C{=}CH_2)_2TeCl_2$ [d] (IIc)	7·54 [e]		6·98 [e]		6·86—7·19, 7·54 [f]	
$(Ph_2C{=}CH_2)_2TeBr_2$ (IIIb)	7·89		7·23	7·46		7·34
$(Ph_2C{=}CH_2)_2TeI_2$ (IIId)	7·74		7·24	7·49		7·35
$(Ph_2C{=}CH_2)_2TeClBr$ (IIIa)	7·93; 7·89		7·23	7·43		7·33
$(Ph_2C{=}CH_2)_2TeClI$ (IIIc)	7·91; [g] 7·87; [g] 7·74 [h]		[i]	7·44		7·33
$(Ph_2C{=}CH)_2Te$ (IVa)	7·49 [j]			7·26 [j]		
$(Tol_2C{=}CH)_2Te$ [k] (IVb)	7·26			7·08 [j]		

[a] δ(Me) 2·23. [b] δ(Me) 2·03 (6H), 2·30 (6H). [c] δ(Me) 2·36, 2·39; δ(Ar) is a multiplet, but in CS_2 at 60 MHz, only two aromatic signals at 7·23 and 7·17 appear. [d] δ(Me) 1·95 (3H), 2·39 (6H), and 2·44 (3H). [e] Two vinylic signals incorporated within aromatic multiplet. [f] Two multiplets centred at 7·54 (t, 3H) and 6·91 (unsym. sextet, 9H). [g] Of equal intensity and give a total of 1H on integration. [h] 1H on integration. [i] Hidden under the aryl signals. [j] Broad signals. [k] δ(Me) 2·32.

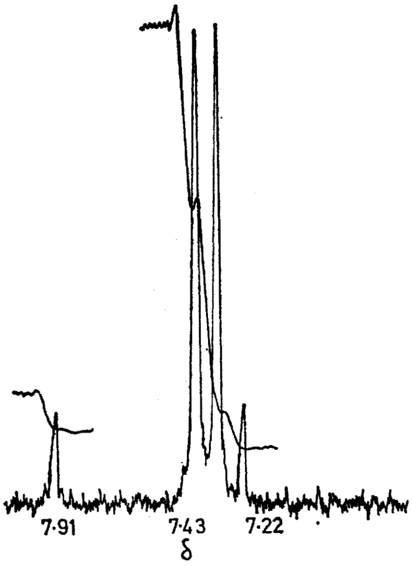

FIGURE 2 N.m.r. spectrum of tellurium dichloride–bis-(1,1-diphenylethylene (IIa)

The following systematic changes are apparent. (*a*) In all shifts H¹ is much more sensitive than H² to structural and environmental changes (temperature, solvent, *etc.*, see below). The same is true for Ar¹ and Ar². (*b*) When for $(Ph_2C{=}CH_2)_2TeX_2$ the halogens are changed from chlorine (IIa) to bromine (IIIb) to iodine (IIId), the H¹ vinylic signals are shifted upfield, and those of Ar¹ are shifted downfield, while the H² and Ar² signals are hardly changed. The shifts between (IIIb) and (IIId) are much larger than between (IIa) and (IIIb). (*c*) In the mixed halides (IIIa and c), H¹ gives two signals of equal intensity, one each at the shifts of the dichloro- (IIa) and the corresponding dihalogeno- (IIIb or d) compound, respectively. In the case of the chloride iodide the lower region signal is a symmetrical doublet with a separation of 0·04 p.p.m. between the lines. (d) In (Ia—c) the vinyl proton signal changes randomly (Ph > Xyl > Tol), while in (IIa—c) the change seems to be systematic (Ph > Tol > Xyl).

Temperature Dependence of the N.m.r. Spectra.—We were interested to find out whether the two types each of vinylic and aromatic protons would merge at higher temperatures, and whether additional multiplicity in vinylic or aromatic signals would appear at lower temperatures as found *e.g.* for the aromatic protons of platinum–pyridine complexes.[14] With various 1,1-diarylethylenes (Ar¹ = Ar²) no splitting of the vinyl signals was observed [15] down to −90 °C. We examined the whole range from −90 to +70 °C with 1,1-diphenylethylene and found neither splitting nor change in the chemical shifts of any of the signals in $[^2H_6]$acetone. The n.m.r. spectra of our tellurium adducts were measured in carbon tetrachloride, from +74 °C down to the freezing point of the solution, or to the point where solute started to precipitate.

The most obvious change observed was in the shift of the H¹ signals, and correspondingly in the difference δ(H¹) − δ(H²). This is shown in Table 4 for (IIa).

Similar changes were observed with the dibromo-compound (IIIb) between −27 [δ(H²) 7·99] and +74 °C [δ(H¹) 7·86) and with the di-iodo-compound (IIId) between −32 [δ(H¹) 7·82] and +45 °C [δ(H¹) 7·73]; in both cases δ(H²) remains practically constant. The average temperature dependency of δ(H¹) per 10 °C is 0·0154 p.p.m. for the

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[14] A. R. Brause, M. Rycheck, and M. Orchin, *J. Amer. Chem. Soc.*, 1967, **89**, 6501.

[15] M. Rabinovitz, I. Agranat, and E. D. Bergmann, *Israel J. Chem.*, 1969, **7**, 795.

dichloride (IIa), 0·0138 for the dibromide (IIIb), and 0·0104 for the di-iodide (IIId).

In these three dihalides the position of phenyl signals is temperature independent but at the lowest temperatures the Ar^1 signal is narrower and higher than that of Ar^2, while on raising the temperature the two become similar and at the highest measured temperatures the Ar^2 signal becomes the narrower and higher one. For the bromo-chloro-compound (IIIa) the H^1 doublet changes from δ 8·05, 8·00 at −20 to 7·90, 7·86 at +55 °C; δ(Ph^1) remains at 7·44, δ(Ph^2) at 7·33, and δ(H^2) changes from 7·23 to 7·21.

Table 4

Temperature dependence of vinyl [δ(H^1), δ(H^2)] and phenyl signals (p.p.m.) for $(Ph_2C{=}CH_2)_2TeCl_2$ (IIa) in CCl_4

T/°C	4·5	9·5	15·0	21·0	26·5
δ(H^1)	7·98	7·97	7·95	7·93	7·92
δ(Ph^1)	7·44	7·43	7·44	7·44	7·44
δ(H^2)	7·33	7·32	7·33	7·32	7·34
δ(Ph^2)	7·22	7·22	7·22	7·22	Hidden

T/°C	31·0	41·0	51·0	62·5	70·0
δ(H^1)	7·92	7·91	7·90	7·89	7·88
δ(Ph^1)	7·43	7·45	7·43	7·42	7·42
δ(H^2)	7·32	7·34	7·32	7·33	7·32
δ(Ph^2)	7·22	7·23	7·22	7·21	7·21

Solvent dependence. On addition of dimethyl sulphoxide (DMSO) to carbon tetrachloride a shift in the values of δ(H^1) and δ(Ph^2) is observed. The shift from one pure solvent to the other is about 1·1 p.p.m. in the H^1 signal and about 0·1 in the Ph^1 signal of (IIa). The effect is obviously a chemical one since the addition of 0·1% (v/v) of DMSO gives about 8% of the total shift, 1% gives 40% of the total change and after 12—14% the change becomes very small (Table 5). The picture is similar in the Ph^1 and Ph^2 signals but merging of the Ph^1, Ph^2, and H^2 signals occurs at higher DMSO concentrations. On removal of the DMSO, the solute was recovered unchanged.

Table 5

Chemical shifts [a] of $(Ph_2C{=}CH_2)_2TeCl_2$ (IIa) in various CCl_4–DMSO mixtures, in p.p.m., at 35 °C

DMSO (%)	0	0·1	0·25	0·5	1	2	3
δ(H^1)	7·91	8·01	8·04	8·24	8·36	8·46	8·54
δ(Ph^1)	7·43	7·48	7·48	7·59	7·54	7·53	7·59
δ(Ph^2)	7·33	7·36	7·38	7·46	7·46	7·45 [b]	7·45 [b]

DMSO %	4	8	12	14	40	80	100
δ(H^1)	8·58	8·69	8·77	8·81	8·89	8·98	9·03
δ(Ph^1)	7·52	7·46	7·51	7·50	7·48	7·51	7·53
δ(Ph^2)	*b*	*b*	*b*	*b*	*b*	*b*	*b*

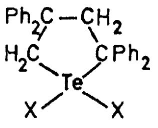
[a] The H^2 signal is incorporated in the Ph^2 multiplet or in the merged Ph^1—Ph^2 multiplet. [b] Multiplet data in the table relate to the highest multiplet. At more than 3% DMSO, the Ph^1 and the Ph^2 signals merge; at more than 40% DMSO, the Ph^1, Ph^2, and H^2 signals become a single broad peak.

In pure carbon disulphide the chemical shifts were the same as in carbon tetrachloride, and on addition of 2% (v/v) of DMSO the δ values for H^1, Ph^1, and H^2 shifted to 8·66, 7·51, and 7·47, respectively. Other aprotic solvents cause lower shifts, *e.g.* 8% (v/v) dimethylformamide in CCl_4 gave δ(H^1) 8·48, δ(Ph^1) 7·51, and δ(Ph^2) 7·43. Acetone (10%) in carbon disulphide gave δ(H^1) 8·28, δ(Ph^1) 7·50, and δ(Ph^2) 7·42; acetonitrile (8%) in carbon tetrachloride gave δ(H^1) 8·18, δ(Ph^1) 7·51, and δ(Ph^2) 7·43. In all cases δ(H^2) seems to coincide with the Ph^2 multiplet.

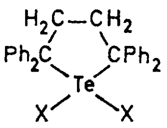
DISCUSSION

Since 1,1-diarylethylenes with different reagents may give a wide variety of products, the structure of compound (II) is not readily predictable. Elemental analysis and n.m.r. spectra strongly suggest the presence of two intact diarylethylene units combined with $TeCl_2$. This structure would represent a completely novel type of bonding between divalent tellurium and a π-donor; therefore it is essential to establish the integrity of the diarylethylene units in (II) and (III). We will endeavour to do this partly by elimination of alternatives and partly by deductions from spectral evidence.

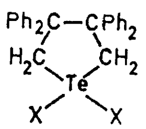
Three types of structures can immediately be eliminated. (*a*) Products of electrophilic ring-telluration, as observed with alkyl aryl ethers and tellurium halides,[16] do not fit the n.m.r. aromatic proton count or its signal multiplicity which establishes that all the protons present originally in (Ia—c) are retained. This is also supported by the mass spectra. (*b*) Structures such as $(Ar_2C{=}CHCl)_2TeH_2$, containing diarylvinyl chloride units or $(Ar_2C{=}CH)_2TeH_2Cl_2$, containing σ-bonded diarylvinyl units are compatible with the elemental analysis, but not with chemical shifts in the n.m.r. spectra. Moreover, the diarylethylene observed in the mass spectra would then require abstraction of a hydrogen atom by a $Ar_2C{=}CH^{+\bullet}$ ion-radical, and such a path is negated by the absence of $Ph_2C{=}CH_2$ in the mass spectrum of $(Ph_2C{=}CH)_2Te$. In addition, the formation of the dimer of $Ph_2C{=}CH_2$ (observed at *m/e* 360) would require a highly improbable complex multi-stage reaction. Since solutions of (IIa) in aqueous acetone are much better conductors than the solvent, and since the halogens they contain are immediately precipitated by $AgNO_3$ and are easily exchanged by different halide ions, structures containing vinylic chlorine atoms are not acceptable. (*c*) Some cyclic structures fit the elemental analysis and the proton count (VIa—c). However, all these contain alicyclic protons which do not agree with the observed chemical shifts. Moreover, the two symmetric cyclic structures should either show a singlet for four apparently equivalent methylenic protons, or signals of higher multiplicity, the nature of which will depend on the conformation of the ring.*



(VIa)



(VIb)



(VIc)

If we accept that the structures contain intact 1,1-di-

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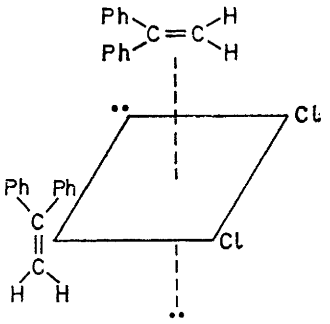
* Consideration of these structures was suggested by a referee.

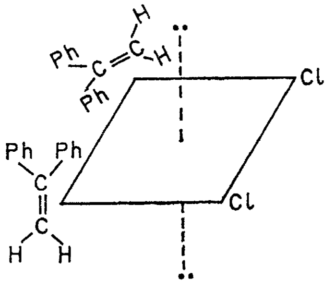
[16] E. Rust, *Ber.*, 1897, **30**, 2828; E. Rohrbaech, *Annalen*, 1901, **315**, 9; K. Lederer, *Ber.*, 1915, **48**, 2049; 1916, **49**, 2532; G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1925, **127**, 2307.

arylethylene units bonded to the tellurium atom, various problems arise as to the nature of the bonding and the stereochemistry in the complexes. In olefin complexes of the transition metals, such as platinum or palladium, π-electron donation from the olefin to the metal and back-donation from the metal to the olefin contribute to the bonding.[17] This is assumed to be responsible for upfield shifts of vinylic protons in the n.m.r. spectrum of the complex, compared with the free olefin.[18] In contrast, compared to (Ia—c) the shift of the vinylic protons in (IIa—c) and (IIIa—d) is strongly downfield, indicating a different type of bonding, probably involving more π-donation.

Structures in which all four aromatic rings and/or all four vinylic protons are equivalent are incompatible with the n.m.r. spectra, which clearly differentiate between two (and only two) types each of aromatic and of vinylic protons, in equal numbers for each case. This also eliminates the possibility of three or four different aromatic and vinylic protons. In order to simplify the discussion we designate the two chemically equivalent units in (IIa) by $Ph^aPh^bC{=}CH^aH^b$ and $Ph^cPh^dC{=}CH^cH^d$. 1,1-Diarylethylenes may apparently act as π-electron donors either through the ethylenic double bond or through the aromatic nuclei, or even through both systems (*e.g.*, acting as a diene towards maleic anhydride),[19] *i.e.* as a bidentate four-electron ligand. However, the bulk of the evidence for π-donor–metal bonding suggests the ethylenic bond as the main reactive site.



(VII)



(VIII)

Two remaining possibilities will be (*a*) two differently bound 1,1-diphenylethylene units in which ($Ph^a = Ph^b$) $\neq$ ($Ph^c = Ph^d$) and ($H^a = H^b$) $\neq$ ($H^c = H^d$) both chemically and magnetically and (*b*), two units bound equally, but with ($Ph^a = Ph^c$) $\neq$ ($Ph^b = Ph^d$) and ($H^a = H^c$) $\neq$ ($H^b = H^d$). The second possibility is less likely, since diarylethylenes in which the two aryl groups are different (*e.g.* Ph and *p*-$Pr^iC_6H_4$–) show splitting of the vinyl signals into a quartet,[15] and in our compounds this was not observed.

With different ligands, widely differing complex structures have been postulated and in some cases proven, *e.g.* urea or thiourea complexes of Te^{II} are square planar.[20,21] The configuration of our complexes derived from Te^{II} implies the distribution of two (I) ligands, two chlorine atoms, and two lone electron pairs of Te in space. The six electron pairs involved may be distributed in octahedral structures. The principal variants are (VII) and (VIII), drawn as the *cis*-isomers, although for complete discussion the *trans*-structures should also be considered.

In (VII) one diphenylethylene (Ia) unit, two chlorine atoms, and a lone pair occupy the equatorial positions, and the second (Ia) unit and the second lone pair the axial ones. The two (Ia) units are unequal and in most conformations the conditions ($Ph^a = Ph^b$) $\neq$ ($Ph^c = Ph^d$) and ($H^a = H^b$) $\neq$ ($H^c = H^d$) will be fulfilled. The nature of the halogens affects the signals somewhat, giving upfield shifts on changing from Cl_2 to Br_2 to I_2. In the mixed halogen derivatives $(Ph_2C{=}CH_2)_2TeClY$ one of the vinyl protons of each (Ia) unit is nearer to Cl and the second nearer to Y, accounting for the observed splitting. In the ClI derivative the lowest field proton is indeed a doublet, although the second low field proton remains a singlet.

In (VIII), which is in fact a square-planar complex, some of the conformations will be symmetrical, while others may contain two nonequivalent ligands, which fit all the features of the n.m.r. spectra discussed above for (VII).

The temperature dependence of the n.m.r. spectra does not help to differentiate between (VII) and (VIII). In (VII) the distances between the ligands are not necessarily equal and some averaging of the signals can be expected by increased thermal vibrations. In (VIII) the average Te–ligand distances may be assumed to be initially equal, and increasing ease of rotation might (though not necessarily) lead to averaging of the signals.

The shifts of the n.m.r. signals on the addition of the dipolar aprotic solvents (see *e.g.* Table 5) is not a simple medium effect, since the main changes occur on the addition of very small amounts. This suggests the

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[17] For references, see R. S. Mulliken and W. B. Person, 'Molecular Complexes,' Wiley–Interscience, New York, 1969, ch. 17 (pp. 271—290).

[18] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 1.

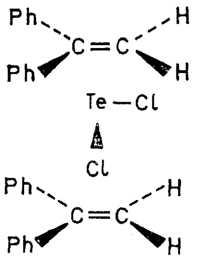
[19] T. Wagner-Jauregg, *Annalen*, 1931, **491**, 1; *Ber.*, 1930, **63**, 3213.

[20] O. Foss, *Acta Chem. Scand.*, 1962, **16**, 779; O. Foss, K. Johnasen, K. Maartmann-Moe, and K. Maroy, *Acta Chem. Scand.*, 1966, **20**, 113.

[21] S. Husebye, *Acta Chem. Scand.*, 1967, **21**, 42.

formation of a fairly stable new complex, in equilibrium with the original, obtained by co-ordination of the dipolar molecule. Indeed, a down-field shift by electron-*attracting* heteroatoms, such as oxygen, is expected and has been observed.[22]

Since the absence of vinylic H^1–H^2 splitting is not unequivocal proof for the equivalence of these two protons, structures in which the two ligands are identical, with each containing two magnetically different protons and two magnetically different aryl groups, cannot be discarded completely. Such structures could consist, for example, of two parallel (or antiparallel) ligands with the $TeCl_2$ sandwiched between them so that the four ethylenic carbon atoms, the tellurium, and one of the chlorine atoms all lie in a single plane while the second chlorine protrudes to one side. Similarly, in any arrangement in which the two ligands are not parallel but their planes form an angle, the Te–H^a and Te–H^b and/or the Cl–H^a and Cl–H^b distances may be different.



Several experiments designed to supply additional information were unfruitful. Ligand-exchange of (IIa) with 1,1-di-(*p*-tolyl)ethylene (Ib) was attempted in order to obtain a complex with two different ligands, but as with *e.g.*, rhodium–ethylene complex,[23] no such exchange occurred. The reaction between 1-*p*-methoxyphenyl-1-phenylethylene and tellurium tetrachloride was tried in order to obtain a complex with two equal ligands containing inherent asymmetry, but this attempt also failed.

The increase in yield on increasing alkylation of the aryl group in $Ar_2C=CH_2$ may point to the electrophilic nature of the initial attack by the tellurium tetrachloride, which could act [24] in the form of $TeCl_3^+Cl^-$. This may also account for the non-reactivity of tellurium dichloride, which was expected to produce, directly, the same complexes as those obtained with the tetrachloride after the loss of two chlorine atoms. This may be due to the peculiar and as yet not completely clarified nature [25] of '$TeCl_2$'.

Owing to the numerous reaction pathways available the product composition changes considerably on relatively minor changes in one of the reactants. For example, tellurium tetrabromide, instead of producing at least some of the $(Ar_2C=CH_2)_2TeBr_2$ complex, gave only a linear dimer [which is a normal product from (Ia) by Lewis-acid catalysis] and a dehydrodimer from (Ib), which is probably formed by dehydrobromination of the dimer formed by the ethylene and the corresponding vinyl halide. The same product has been obtained from (Ib) and bromine,[26] and the analogous 1,1,4,4-tetrakis-*p*-methoxyphenylbuta-1,3-diene from 1,1-bis-(*p*-methoxyphenyl)ethylene and bromine.[27]

$$\mathrm{Tol_2C{=}CH_2 + TeBr_4 \longrightarrow Tol_2C{=}CHBr \xrightarrow[-HBr]{Tol_2C=CH_2} Tol_2C{=}CH{=}CH{=}CTol_2}$$

EXPERIMENTAL

Instrumentation.—The following instruments were used: i.r., Perkin-Elmer 337; u.v., Perkin-Elmer 450 and Unicam SP 800; n.m.r., Varian HA-100 MHz and T-60 MHz; and mass spectrometers, Atlas C-4 and MAT CH-5.

Materials.—1,1-Diphenylethylene,[28] 1,1-di-*p*-tolylethylene,[29] and 1,1-diphenylpropene [30] were prepared as described in the literature. 1,1-bis-(2,4-dimethylphenyl)-ethylene [29] was distilled *in vacuo* and solidified after cooling; m.p. 42° (from ethanol). Commercial tellurium tetrachloride and tetrabromide (Schuchard, Munchen) and tellurium dichloride and dibromide (City Chemical Corp., New York) were used.

Tellurium Dichloride–Bis-(1,1-*diphenylethylene*) (IIa).—Tellurium tetrachloride (10 g) in dry ether (25 ml) was added to a solution of 1,1-diphenylethylene (Ia) (10 g) in ether (25 ml). The mixture was stirred for 5 h at room temperature, then left overnight. The precipitate was filtered off, washed with ether, and recrystallized from n-butanol or carbon tetrachloride to yield *needles* (1·5 g, 9·7%), m.p. 230—232° (Found: C, 60·5; H, 4·4; Cl, 12·9; Te, 23·0. $C_{28}H_{24}TeCl_2$ requires C, 60·15; H, 4·3; Cl, 12·7; Te, 22·85%). Use of a larger excess of (Ia), or solutions of the reactants in other solvents (tetrahydrofuran, acetonitrile, dimethylformamide, dimethyl sulphoxide, or ethylene carbonate) either lowered the yield or gave no (IIa) and only unchanged (Ia), its various dimers, and some 2-chloro-1,1-diphenylethylene.

The mother liquor from (IIa) was treated with water (20 ml) (in order to decompose the excess of tellurium tetrachloride) and chloroform (50 ml). The organic fraction was dried (Na_2SO_4) and evaporated, and the residue crystallized from ethanol to give 1,1,3,3-tetraphenylbut-1-ene (40%), m.p. and mixed m.p. 112° (lit.,[6] 112°); δ (CCl_4) 7·33 (20H, aryl), 6·94 (1H, vinyl), and 1·50 (3H, Me).

Attempted synthesis of (IIa) in refluxing carbon tetrachloride or dioxan yielded only 1,1,3,3-tetraphenylbut-1-ene (70%).

A mixture of tellurium tetrachloride (5 g) and 1,1-diphenylethylene (Ia) (12 g) without solvent gave an exo-

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[22] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, London, 1966, vol. 2, p. 670.

[23] M. L. H. Green, 'The Transition Elements' (' Organometallic Compounds,' vol. 2), Methuen, London, 3rd edn., 1968, p. 22.

[24] H. Gerdin and H. Houtgraaf, *Rec. Trav. chim.*, 1954, **73**, 737; N. Katsaros and J. W. George, *Inorg. Chim. Acta*, 1969, **3**, 165.

[25] E. E. Aynsley, *J. Chem. Soc.*, 1953, 3016.

[26] O. Schmitz-Dumont, K. Thomke, and H. Diebold, *Ber.*, 1937, **70***B*, 175.

[27] F. Bergmann, J. Szmuskovicz, and E. Dimant, *J. Amer. Chem. Soc.*, 1949, **71**, 2968.

[28] C. F. H. Allen and S. Converse, *Org. Synth.*, 1941, **1**, 226.

[29] A. Bistrzycki and E. Reintke, *Ber.*, 1905, **38**, 839.

[30] A. Klages, *Ber.*, 1902, **35**, 2646.

thermic reaction on stirring, and after about 10 min the mixture solidified. Crystallisation from n-butanol or ethanol yielded the cyclic dimer 3-methyl-1,1,3-triphenylindane (7·6 g, 63%), m.p. and mixed m.p. 145° (lit.,[6] 145°), δ (CCl_4) 7·10, 7·18, and 7·24 (19H, aryl), 2·94, 3·13, 3·35, and 3·54 (2H, methylene ABq), and 1·53 (3H, Me).

Attempted Preparation of the Bromine Analogue (IIIb).—1,1-Diphenylethylene and tellurium tetrabromide under the various experimental conditions mentioned for (Ia) yielded no adduct. In refluxing carbon tetrachloride 1,1,3,3-tetraphenylbut-1-ene was obtained (57%) and identified as above.

Other Attempted Routes to (IIa) *and* (IIIb).—Compound (Ia) and tellurium dichloride or tellurium dibromide under various conditions, yielded no (IIa) or its bromine analogue (IIIb). The only product obtained was in all cases 1,1,3,3-tetraphenylbut-1-ene (*ca.* 15%), and most of (Ia) was recovered unchanged.

Tellurium Dichloride–Bis-(1,1-*di*-p-*tolylethylene*) (IIb).—In ether, as described for (IIa), the *product* (IIb) from 1,1-di-*p*-tolylethylene and tellurium tetrachloride was obtained in 19% yield, m.p. 225—226° (from n-butanol or carbon tetrachloride) (Found: C, 62·6; H, 4·85; Cl, 11·9; Te, 21·45. $C_{32}H_{32}TeCl_2$ requires C, 62·5; H, 5·25; Cl, 11·5; Te, 20·75%). The mother liquor contained mainly unchanged 1,1-di-*p*-tolylethylene and some 1,1,3,3-tetra-*p*-tolylbut-1-ene which was not isolated but identified by its n.m.r. spectrum (see below).

Without a solvent, tellurium tetrachloride (3 g) and 1,1-di-*p*-tolylethylene (6 g) were heated on a water-bath with stirring for 15 min, after which time the mixture solidified. Work-up gave 1,1,3,3-tetra-*p*-tolylbut-1-ene (3·2 g, 53%), m.p. 105—107° (lit.,[26] 107°) (Found: C, 92·3; H, 7·7; Calc. for $C_{32}H_{32}$: C, 92·25; H, 7·75%), δ (CCl_4) 7·04 and 7·02 (16H, aryl), 6·34 (1H, vinyl); 2·17 and 2·14 (12H, MeC_6H_4), and 1·18 (3H, Me in chain), $\lambda_{max.}$ ($CHCl_3$) 256 nm (ε 16,700), $\lambda_{max.}$ (MeCN) 259·5 nm (ε 16,200).

Reaction of Tellurium Tetrabromide with 1,1-*Di*-p-*tolylethylene*.—Tellurium tetrabromide (3 g) and 1,1-di-*p*-tolylethylene (2·5 g) in dry ether (20 ml) were stirred for 4 h and left overnight. Work-up as usual gave no tellurium-containing material. The oil obtained solidified on treating with light petroleum, and was crystallized from n-butanol, giving the dehydrodimer of the starting material, 1,1,4,4-tetra-*p*-tolylbuta-1,3-diene (38%), m.p. 255° (lit.,[26] 248°) (Found: C, 92·35; H, 7·3. Calc. for $C_{32}H_{30}$: C, 92·7; H, 7·3%), δ 7·16 and 7·0 (8H, aryl), 6·67 (2H, vinyl), and 2·39 and 2·28 (6H, Me).

Tellurium Dichloride–Bis-[1,1-*bis*(2,4-*dimethylphenyl*)-*ethylene*] (IIb).—Tellurium tetrachloride (2·5 g) and 1,1-bis-(2,4-dimethylphenyl)ethylene (3·5 g) in ether (25 ml), under the conditions described for the preparation of (IIa), yielded the *product* (IIb) (1·7 g, 36%), m.p. 215° (from n-butanol or carbon tetrachloride) (Found: C, 63·95; H, 5·85; Cl, 11·1; Te, 19·1. $C_{36}H_{40}TeCl_2$, requires C, 64·4; H, 6·0; Cl, 0·5; Te, 19·0%). We were unable to isolate any dimer from the mother liquor, nor to detect its presence by n.m.r. spectroscopy.

Tellurium Chloride Iodide–Bis-(1,1-*diphenylethylene*) (IIIc).—This was prepared from (IIa) (0·56 g, 0·001 mol) and potassium iodide (0·167 g, 0·001 mol) in acetonitrile (20 ml). The mixture was stirred for 15 h and refluxed for 1 h. Water (20 ml) and chloroform (40 ml) were added and the organic layer was separated, dried (Na_2SO_4), and evaporated. The residue (0·48 g, 74%) yielded dark yellow *crystals*, m.p. 196—198° (from carbon tetrachloride) (Found: C, 51·4; H, 3·2; Cl, 6·0; I, 20·85; Te, 20·2. $C_{28}H_{24}TeClI$ requires C, 51·7; H, 3·7; Cl, 5·45; I, 19·5; Te, 19·6%). The same procedure, with twice the amount of potassium iodide, yielded red crystals (0·57 g, 67%) of *tellurium di-iodide–bis-*(1,1-*diphenylethylene*) (IIId), m.p. 189—190° (Found: C, 45·35; H, 3·0; I, 33·75; Te, 16·6. $C_{28}H_{24}TeI_2$ requires C, 45·3; H, 3·25; I, 34·2; Te, 17·2%). Similarly, (IIa) and potassium bromide refluxed for 4 h and stirred overnight, yielded yellow *tellurium bromide chloride–bis-*(1,1-*diphenylethylene*) (IIIa) (61%), m.p. 234—235° (from carbon tetrachloride) (Found: C, 55·65; H, 3·95; Br + Cl (determined as Br) 26·0. $C_{28}H_{24}TeClBr$ requires C, 55·8; H, 4·0; Br + Cl together as Br, 26·20%. Use of twice the amount of potassium bromide gave *tellurium dibromide–bis-*(1,1-*diphenylethylene*) (IIIb) (43%) m.p. 241° (from carbon tetrachloride) (Found: C, 52·15; H, 3·4; Br, 25·15%; Te, 19·25. $C_{28}H_{24}TeBr_2$ requires C, 51·9; H, 3·75; Br, 24·65; Te, 19·7%).

Attempted Preparation of Tellurium Difluoride–Bis-(1,1-*diphenylethylene*).—Use of an excess of potassium fluoride in the procedure as above gave a compound which gave n.m.r. and mass spectra compatible with tellurium difluoride–bis-(1,1-diphenylethylene), but the elemental analyses were not consistent with this and repeated preparations gave widely varying values. This product was not studied further; δ (CCl_4) 7·42 (10H, aryl), 7·32 (10H, aryl), 7·95 (2H, vinyl), and 7·21 (2H, vinyl); mass spectrum molecular ion for ^{130}Te *m/e* 528 (total 0·5%), base peak *m/e* 178 (Ph_2C_2); $\lambda_{max.}$ ($CHCl_3$) 300 nm (ε 20,500); $\lambda_{max.}$ (MeCN) 292 nm (ε 20,200)].

Reaction of (IIa) *with Mercury*(II) *Acetate*.—Compound (IIa) (0·5 g, 0·001 mol) and mercury(II) acetate (0·32 g, 0·001 mol) in acetonitrile (25 ml) were refluxed for 5 h and left overnight. The product, (2,2-diphenylvinyl)mercury-(II) chloride crystallized from benzene; m.p. 140° (yield 88%) and was identified by m.p., mixed m.p.,[2] analysis, and n.m.r. and mass spectra (Found: C, 40·1; H, 2·45; Cl, 8·25. Calc. for $C_{14}H_{11}ClHg$: C, 40·05; H, 2·65; Cl, 8·55%), δ (CCl_4) 7·32 and 7·18 (10H, aryl) and 6·31 (1H, vinyl).

Dehydrochlorination of (IIa).—A solution of (IIa) (0·44 g) in carbon tetrachloride (10 ml) was mixed with a solution of potassium disulphite (1 g) in water (10 ml) and refluxed for 2 h. Traces of tellurium precipitated. After cooling, the dried organic layer yielded a yellow powder (0·31 g, 80%) which gave yellow crystals, m.p. 119—120° (from carbon tetrachloride) of *bis-*(2,2-*diphenylvinyl*) *telluride* (Found: C, 68·95; H, 4·2; Te, 26·2. $C_{28}H_{22}Te$ requires C, 69·2; H, 4·55; Te, 26·25%). The same product was also obtained from (IIa) and methylmagnesium bromide in ether, under nitrogen, in 78% yield (same m.p., analyses, and n.m.r. spectrum).

Dehydrochlorination of (IIb).—The same procedure as described for (IIa), yielded from (IIb) (0·425 g) *bis-*(2,2-*di*-p-*tolylvinyl*) *telluride* (56%), m.p. 173—175°, after precipitation from carbon tetrachloride by light petroleum, in the form of a yellow microcrystalline powder (Found: C, 70·65; H, 5·7; Te, 23·55. $C_{32}H_{30}Te$ requires C, 70·9; H, 5·55; Te, 23·55%).

Chlorination of (IIa).—Chlorine was passed through a solution of (IIa) (0·4 g) in hot carbon tetrachloride (20 ml) until no more precipitate formed. The crystals consisted of tellurium tetrachloride while the solution contained mainly 2-chloro-1,1-diphenylethylene, identified by comparison of its n.m.r. spectrum [δ 6·31 (vinyl)] with that of an authentic sample obtained by chlorination of 1,1-diphenylethylene.[31]

Chlorination of (IIb).—Treatment of (IIb) as for (IIa), yielded tellurium tetrachloride and 2-chloro-1,1-di-*p*-tolylethylene, m.p. 64° (lit.,[31] 67°), δ (CCl_4) 7·08 and 6·97 (8H, aryl), 6·38 (1H, vinyl), and 2·34 and 2·28 (6H, Me).

Reaction of (IIa) *with Butyl-lithium*.—A solution of butyllithium (1N; 2·2 ml) was added under nitrogen to (IIa) (0·56 g) in dry ether (25 ml), and the mixture was stirred for 3 h. Water (25 ml) and chloroform (50 ml) were added and the organic layer was separated, dried, and evaporated. The residue was 1,1,4,4-tetraphenylbuta-1,3-diene (0·136 g, 38%), m.p. 205° (from toluene) (lit.,[32] 201—202), identified by its u.v.[33] and n.m.r. spectra: δ (CCl_4) 7·20 and 7·43 (20H, aryl) and 6·88 (2H, vinyl).

Attempted Ligand-exchange in (IIa).—(a) *In cold homogeneous solution*. The n.m.r. spectrum of a solution of (IIa) (5 mg) and $Tol_2C{=}CH_2$ (45 mg) in carbon tetrachloride (0·5 ml) showed only the characteristic signals of the two solutes, and no signals corresponding to free 1,1-diphenylethylene or to $(Tol_2C{=}CH_2)_2TeCl_2$.

(b) *In partly heterogeneous conditions*. Compound (IIa) (500 mg) and $Tol_2C{=}CH_2$ (2·1 g) in carbon tetrachloride (25 ml) were refluxed [most, but not all of (IIa) dissolved] for 2 h. The reagents were recovered unchanged as shown by n.m.r. analysis.

Stability of (IIa).—The adduct is light-sensitive and after a few min in indirect light (faster when exposed to direct sunlight) it becomes red and then black. In the absence of light it is stable when refluxed in acetone–water (1 : 1), carbon tetrachloride, or chlorobenzene for 15 h or in pure triethylamine for 2 h. In all cases the bulk of (IIa) was recovered unchanged, although traces of tellurium precipitated.

Unsuccessful Experiments with Tellurium Tetrachloride.—1-*p*-methoxyphenyl-1-phenylethylene, 1,1-bis-(*p*-methoxyphenyl)ethylene, and 1,1-bis-(2,3-dimethylphenyl)ethylene gave only intractable black gums on treatment with tellurium tetrachloride.

Reaction of $TeCl_4$ *with* 1,1-*Diphenylpropene*.—To 1,1-diphenylpropene (3·9 g, 0·02 mol) in carbon tetrachloride (25 ml), tellurium tetrachloride (5·4 g, 0·02 mol) was added and the mixture was refluxed for 3 h. Crystals (3·5 g) were obtained and recrystallized from butanol, giving 2-methyl-1,1,3,3-tetraphenylpropene (3·1 g, 86%), m.p. 128° (lit.,[10] 132—133°) (Found: C, 93·15; H, 6·6. Calc. for $C_{28}H_{24}$: C, 93·3; H, 6·7%), δ (CCl_4) 1·63 (3H, s, Me), 5·23 (1H, s, =CH), and 7·17br (20H, s, Ph_4); i.r. spectrum very similar to that of 1,1,3,3-tetraphenylbut-1-ene, with small differences in the fingerprint region; $\lambda_{max.}$ (MeCN) 222 nm (ε 23,500) and 237sh nm (ε 16,000), *m/e* 360 (M^+, 61%), 165 (100%, fluorenyl cation?), 167 (56%, Ph_2CH^+), and other peaks at $M - CH_3$ and at $M - C_2H_5$.

Reaction of $TeCl_4$ *with Styrene*.—To styrene (2 g, 0·02 mol) in dry ether (25 ml), tellurium tetrachloride (5·4 g, 0·02 mol) was added. When the initially exothermic reaction subsided, the mixture was stirred for 1 h and left overnight. The precipitate yielded white crystals (1·6 g, 36%), m.p. 176—178° (from n-butanol) (Found: C, 43·7; H, 3·55; Cl, 23·3. $C_{16}H_{14}Cl_3Te$ requires C, 43·65; H, 3·2; Cl, 24·5%), δ ($CDCl_3$) 3·50—4·33 (2H, m), 5·00—5·66 (2H, unsym. sextet), and 7·33br (10H, s, Ph_2). The mass spectrum, in the area expected for the molecular ion gives a multiplicity of lines, including *m/e* 441 (0·1%, corresponding mainly to $R^{130}Te^{35}Cl_3$ and $R^{128}Te^{35}Cl_2{}^{37}Cl$). The base peak is at *m/e* 206 ($M - TeCl_3$). Other peaks occur at $M - Cl$ (m, total for all isotopes about 10%).

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