

Reactions of Tellurium(IV) Halides with Anthracene and Other Organic Compounds

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The reactions of TeX_4 (where X = Cl, Br, or I) and $\text{R}_n\text{TeX}_{4-n}$ (where R = Ph or *p*-MeO-C₆H₄ and *n* = 1 or 2) with benzene, anthracene and its halogenated derivatives, 1,1-diphenylethylene, and triphenylphosphine have been investigated. Factors directing the reaction to telluration or chlorination are considered.

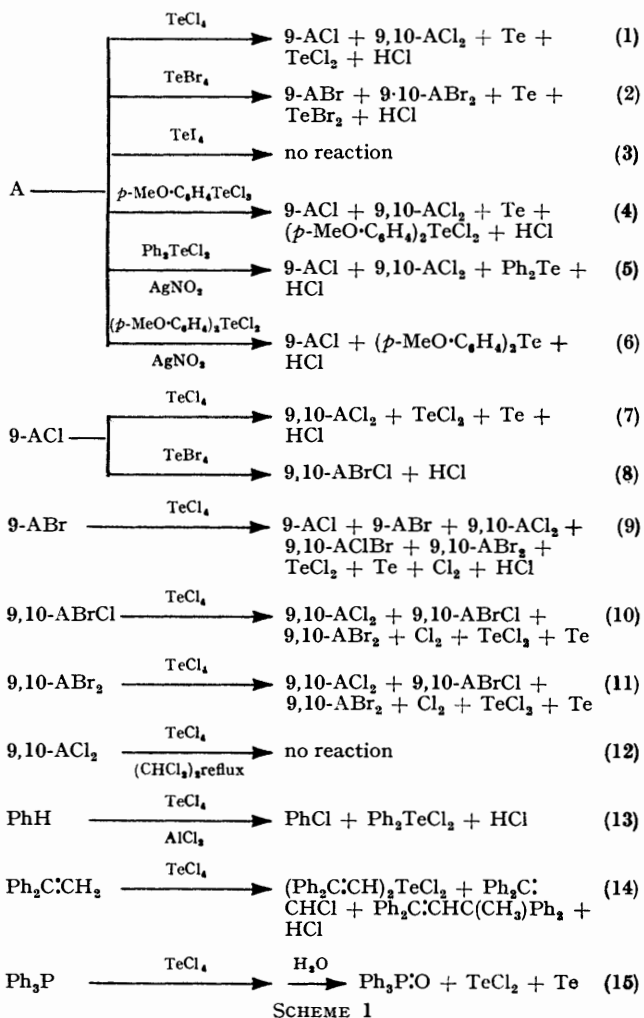
REACTIONS of Te^{IV} compounds with organic substrates have been known since 1826.¹ They have been reviewed by Rheinboldt,² by Petragnani and Campos,³ and in a monograph edited by Cooper.⁴ Most of the work in this area has been carried out from the point of view of synthetic utility. Several authors have reported contradictory results on the same reactions. Fischer *et al.*⁵ reported the decomposition of TeCl_4 in the presence of cyclohexene and the formation of elemental tellurium. Petragnani *et al.*,^{6,7} Funk *et al.*,⁸ and Ogawa *et al.*⁹ found an addition reaction of TeCl_4 to cyclohexene. Fischer⁵ and Petragnani⁶ observed unidentified chlorination products in the reaction between styrene and TeCl_4 . For the same reaction Patai and Elmaleh¹⁰ claimed telluration of styrene. Sadikov *et al.*¹¹ reported the telluration of naphthalene, anthracene, pyrene, and fluorene, whereas in our work with anthracene under the same experimental conditions (see later) only chlorination of anthracene was detected. Morgan *et al.*¹² claimed telluration of acetone with TeCl_4 whereas Rust¹³ had not succeeded in obtaining an acetone telluration product. However with acetophenone in ether a telluration product was isolated. The present results show the decomposition of TeCl_4 in the presence of acetone.

For the telluration reactions of unsaturated organic systems a mechanism involving attack by TeX_3^+ on the unsaturated system was suggested.^{3,6} However no general hypothesis covering the different modes of reactions of TeX_4 with different substrates and under varying conditions has as yet been put forward. We suggest here a general binding model for tellurium compounds of the type $\text{R}_n\text{TeX}_{4-n}$ where R is an organic residue and X a halogen atom. This model explains the influence of factors such as polarity of solvent and nature of R and X on the ambident electrophilic reactivity of these compounds (telluration *vs.* chlorination).

RESULTS

The reactions between equimolar quantities of TeX_4 (where X = Cl, Br, or I) or $\text{R}_n\text{TeX}_{4-n}$ (R = Ph or *p*-MeO-C₆H₄, *n* = 1 or 2) and anthracene (A), 9-chloroanthracene

(9-ACl), 9-bromoanthracene (9-ABr), 9,10-dibromoanthracene (9,10-ABr₂), 9-bromo-10-chloroanthracene (9,10-ABrCl), benzene, 1,1-diphenylethylene, and triphenylphosphine are summarized in Scheme 1. Reactions (1) and (2)



SCHEME 1

were accelerated by catalytic quantities of AlCl_3 . In cases (5) and (6) there was no reaction in the absence of catalysis by Ag^+ . The yields of the reaction products are given in Table I.

⁸ H. Funk and W. Weiss, *J. prakt. Chem.*, 1954, **4**, 33.

⁹ M. Ogawa and R. Ishioka, *Bull. Chem. Soc. Japan*, 1970, **43**, 496.

¹⁰ D. Elmaleh, S. Patai, and Z. Rappoport, *J. Chem. Soc. (C)*, 1971, 3100.

¹¹ I. D. Sadikov and V. I. Minkin, *Zhur. obshchei Khim.*, 1972, **42**, 2713.

¹² G. T. Morgan and G. C. Elvins, *J. Chem. Soc.*, 1925, 2627.

¹³ E. Rust, *Ber.*, 1897, **30**, 2833.

¹ J. J. Berzelius, *Prog. Ann.*, 1826, **8**, 411.

² H. Rheinboldt, in Houben-Weyl, 'Methoden der Organischen Chemie,' Thieme, Stuttgart, 1955, vol. IX, p. 1048.

³ N. Petragnani and M. De M. Campos, *Organometallic Chem. Rev.*, 1967, **2**, 61.

⁴ W. C. Cooper, 'Tellurium,' Van Nostrand-Reinhold, New York, 1971, (a) p. 146; (b) p. 225; (c) p. 145; (d) pp. 139, 249; (e) pp. 239, 241, 245.

⁵ C. H. Fischer and A. Eisner, *J. Org. Chem.*, 1941, **6**, 169.

⁶ N. Petragnani and M. De M. Campos, *Tetrahedron*, 1962, **18**, 521.

⁷ N. Petragnani and M. De M. Campos, *Tetrahedron Letters*, 1959, 11.

TABLE 1

Yields of principal products of reactions of $\text{Ar}_n\text{TeX}_{4-n}$ with anthracene and halogenoanthracenes (Scheme 1)

Reaction (1)–(4)	Yield (%) ^a				
	9-ACl	9,10-ACl ₂	9-ABr	9,10-ABr ₂	9,10-ABrCl
(5)	60	Trace	See Table 2		
(6)	42				
(7)		100			
(8)					Trace
(9) ^b	22	53	8	5	12
(9) ^c	2	89	Trace	3	6
(10) ^d		69		8	23
(10) ^e		97		Trace	2
(11) ^e		51		29	20
(11) ^e		96		Trace	4

^a Based on initial amount of anthracene. ^b After 7 h. ^c After 24 h. ^d After 9 h. ^e After 4 h.

The reaction (14) between 1,1-diphenylethylene and TeCl_4 was sensitive to the solvent used. With Et_2O the yield of $(\text{Ph}_2\text{C}:\text{CH})_2\text{TeCl}_2$ was 20% whereas with CCl_4 , CHCl_3 , CH_2Cl_2 , or PhH this product was absent. In the reaction (15) between Ph_3P and TeCl_4 , $\text{Ph}_3\text{P}:\text{Cl}_2$ is assumed to be the intermediate which is hydrolysed to $\text{Ph}_3\text{P}:\text{O}$. No products of telluration of the phosphorus were detected, in contrast to findings in the reactions between phosphines and elemental tellurium.³

With 9-ABr and TeCl_4 [reaction (9)] 9-ACl and 9,10-ABrCl are the main products at the beginning of the reaction with the former preponderant (ratio 4 : 1). As the reaction

the amount of 9,10-ABrCl decreases, being converted into 9,10-ACl₂.

The reactions between anthracene and TeCl_4 (1), TeBr_4 (2), and $p\text{-MeO}\cdot\text{C}_6\text{H}_4\text{TeCl}_3$ (4) were subjected to a more detailed study of the influence of solvent polarity. Results are presented in Table 2.

In the reactions in dioxan and in ether (runs 8 and 10 in Table 2) an adduct of TeCl_4 and the solvent was isolated (an adduct with ether was also reported by Morgan¹⁴ and Rust¹⁵). The formation of such adducts is accompanied by repression of the reactions. For CCl_4 , CHCl_3 , and CH_2Cl_2 (runs 1–3) an increase in yield (under the same experimental conditions) is observed with increase in polarity of the solvent. A parallel behaviour was found for the initial rates of the reaction in different solvents, *i.e.* CH_2Cl_2 , CHCl_3 , CCl_4 , PhMe, and PhH in decreasing order.

We found that under identical conditions the reactivities of the tellurium tetrahalides increase in the order $\text{TeCl}_4 > \text{TeBr}_4 > \text{TeI}_4$. The same order was observed by Petrag-nani¹⁶ for compounds of the type ArTeX_3 .

In the reactions between TeCl_4 or $p\text{-MeO}\cdot\text{C}_6\text{H}_4\text{TeCl}_3$ and Ph_3P , anthracene, 1,1-diphenylethylene, and many other olefins a solvent-dependent intense colour was initially formed which faded with time. In the reaction between TeCl_4 and anthracene in benzene the absorption spectrum of the solution showed two broad peaks at 465 and 760 nm. Similar colours are produced in toluene, *p*-xylene, methylene chloride, chloroform, and carbon tetrachloride, but not in dioxan or diethyl ether. The broadness of the peaks

TABLE 2

Influence of solvent on the reaction between equimolar quantities of anthracene and TeCl_4 , TeBr_4 , or $p\text{-MeO}\cdot\text{C}_6\text{H}_4\text{TeCl}_3$

Run no.	Solvent	T/°C	t/h	Yield ^a (%)	9,10-AX ₂	
					9-AX + 9,10-AX ₂	9-AX + 9,10-AX ₂
TeCl₄						
1	CCl_4	0	4	26	0	1
2	CHCl_3	0	4	60	0	1
3	CH_2Cl_2	0	4	96	0	1
4	CH_2Cl_2	Reflux	7	100	0.93	0.07
5	CHCl_3	Reflux	14	100	0.86	0.14
6	CCl_4	Reflux	14	100	0.59	0.41
7 ^b	PhMe	Reflux	4	73	0.06	0.94
8	Dioxan	27	72	0	0	0
9	Dioxan	105	72	56	0.36	0.64
10	Et_2O	0	14	0	0	0
11	Et_2O	25	14	16	0	1
TeBr₄						
12	PhMe	110	72	18	0	1
13	$(\text{CHCl}_2)_2$	110	72	42	0.16	0.84
14	Dioxan	70	120	0	0	0
<i>p</i>-MeO·C₆H₄TeCl₃						
15	PhMe	105	60	26	0	1
16	$(\text{CHCl}_2)_2$	105	60	58	0.18	0.82

^a Calculated on the base of anthracene consumed. ^b Performed under the experimental conditions given in ref. 11.

proceeds the amount of 9,10-ACl₂ increases and the amounts of other halogenated anthracenes decrease. With 9,10-ABrCl and TeCl_4 [reaction (10)] 9,10-ACl₂ is formed rapidly and after 24 h becomes the main product (all other dihalogenated anthracenes diminish to trace amounts). With 9,10-ABr₂ and TeCl_4 [reaction (11)] the amount of 9,10-ABr₂ decreases, while the amounts of 9,10-ACl₂ and 9,10-ABrCl increase with 9,10-ACl₂ predominating. After 14 h 9,10-ABr₂ has been consumed almost completely. At this stage

formed and the difference between their wavelengths, which fits the energy difference between the HOMO and the next MO of anthracene,¹⁷ together with the fact that only anthracene with its lower ionization potential (as opposed to halogenated anthracenes) and TeCl_4 and ArTeCl_3 with their higher electron affinities (as opposed to TeBr_4) gave the colour, suggest the formation of a charge-transfer complex in these cases. This agrees with the fact that in solvents of

¹⁶ N. Petrag-nani, *Tetrahedron*, 1961, **12**, 219.

¹⁷ R. Foster, 'Organic Charge Transfer Complexes,' Academic Press, London and New York, 1969, p. 68.

¹⁴ G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1925, 2307.

¹⁵ E. Rust, *Ber.*, 1897, **30**, 2828.

co-ordinating ability such as ether or dioxan no colour appeared.

Analysis of the inorganic residue from these reactions (see Experimental section) suggests that it is composed of a mixture of Te and TeX_2 , the former being formed by disproportionation of TeX_2 to Te and TeX_4 ^{18,19} which is partly or wholly consumed in the reaction.

A similar disproportionation explains the formation of Te and $(p\text{-MeO}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2$ in the reaction of $p\text{-MeO}\cdot\text{C}_6\text{H}_4\text{-TeCl}_3$ with anthracene. $(p\text{-MeO}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2$ is inactive as a chlorinating or tellurating agent as was confirmed in independent experiments [reactions (5) and (6)].

DISCUSSION

X-Ray data for some compounds R_2TeX_2 show two unequal apical Te-X bonds.²⁰ X-Ray data for TeCl_4 ²¹ and $\text{ClCH}_2\text{-CH}_2\text{-TeCl}_3$ ²² also show that one of the Te-X bonds in each of these molecules is longer than the others. I.r. and Raman analysis of TeX_4 and its derivatives²³⁻²⁷ led to the assumption of a TeX_3^+X^- structure with some kind of transfer of charge from X^- to TeX_3^+ ²⁷ for TeX_4 in the solid state and in solution.

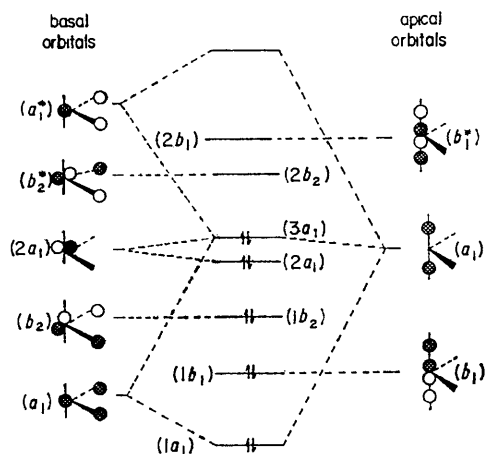


FIGURE 1 Molecular orbitals of TeX_4 in C_{2v} symmetry

Electron diffraction analysis of TeCl_4 in the gas phase²⁸ showed an additional shoulder at 2.75 Å which, it seems to us, may be explained in terms of one longer Te-Cl bond.

On the basis of a bonding model for a hypothetical structure of TeX_4 in C_{2v} symmetry, which is derived from a trigonal bipyramidal geometry with the lone electron pair occupying an equatorial position, it is shown below that distortion of this geometry by lengthening one Te-X bond leads to stabilization. Such a bonding model of TeX_4 without the participation of $5d$ orbitals can be constructed according to Hoffman²⁹ and Rundle³⁰ ($4f$ orbitals are not considered here). Thus the molecular

¹⁸ O. Foss, *Pure Appl. Chem.*, 1970, **24**, 31.

¹⁹ E. E. Aynsley, *J. Chem. Soc.*, 1953, 3016.

²⁰ G. C. Hayward and P. J. Hendra, *J. Chem. Soc. (A)*, 1969, 1761.

²¹ B. Buss and B. Kerbs, *Inorg. Chem.*, 1971, **10**, 2795.

²² D. Kobelt and E. F. Paulus, *Angew. Chem. Internat. Edn.*, 1971, **10**, 74.

²³ N. N. Greenwood, B. P. Straughan, and A. Wilson, *J. Chem. Soc. (A)*, 1968, 2209.

²⁴ G. C. Hayward and P. J. Hendra, *J. Chem. Soc. (A)*, 1967, 643.

orbitals shown in Figure 1 are obtained from sets of apical and basal orbitals of TeX_4 .

As can be deduced from the interactions detailed in Figure 1, orbital $3a_1$, which is the HOMO, has the nodal structure shown in Figure 2, and is slightly antibonding.

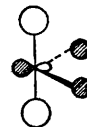


FIGURE 2 $3a_1$ Orbital of TeX_4

This orbital may be stabilized by interaction with $5d$ orbitals of the same symmetry, by appropriate distortion from C_{2v} symmetry, or by both processes. One such distortion of the molecule is elongation of one of the Te-X bonds leading to a $\text{TeX}_3^{\delta+}\cdots\text{X}^{\delta-}$ structure and this is in accord with the above mentioned data. The stabilization gained by this distortion can be seen from the correlation diagram (Figure 3) describing the $\text{TeX}_4 \rightarrow \text{TeX}_3 + \text{X}$ process (the elongation of the Te-X bond is along the X axis; σ_{xz} is conserved; MOs of TeX_3 are constructed with assumption of C_{3v} symmetry) in which at the extreme cleavage of the bond occurs.

In molecules of the type TeX_2Y_2 of bipyramidal structure the more electronegative groups are expected to occupy the apical positions, which are the positions of

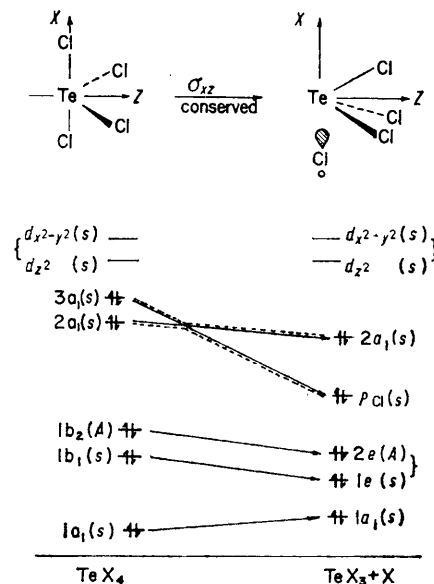


FIGURE 3 Correlation diagram describing the $\text{TeX}_4 \rightarrow \text{TeX}_3 + \text{X}$ process

higher electron density as can be seen in Figure 1. This expectation is confirmed by X-ray and spectral data for a

²⁵ N. Katsaros and J. W. George, *Inorg. Chim. Acta*, 1969, **3**, 165.

²⁶ D. M. Adams and P. J. Lock, *J. Chem. Soc. (A)*, 1967, 145.

²⁷ N. N. Greenwood, B. P. Straughan, and A. Wilson, *J. Chem. Soc. (A)*, 1966, 1479.

²⁸ D. P. Stevenson and V. Schoemaker, *J. Amer. Chem. Soc.*, 1940, **62**, 1267.

²⁹ R. Hoffman, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 3047.

³⁰ R. E. Rundle, *Rec. Chem. Progr.*, 1962, **23**, 195.

number of compounds R_2TeX_2 .^{20,31-33} The above model and the ensuing discussion are also applicable to the isomorphous SeX_4 compounds.^{24,34} From the correlation diagram (Figure 3) it can be seen that, depending upon identity of substituents and environment, the whole spectrum of structures between TeX_4 and $TeX_3^+ + X^-$ can be expected. Similarly the chemical behaviour of the compounds TeX_4 and $RTeX_3$ will vary with structure and reaction conditions and the molecules will evince either donor or acceptor properties as follows.

(a) TeX_4 and $RTeX_3$ are Lewis bases in the presence of Lewis acids such as ^{26,35} $AlCl_3$, AsF_5 , and $SbCl_5$. These react with TeX_4 to give 1 : 1 adducts which behave as salts in solution.^{26,35,36} X-Ray analysis of the solid $TeCl_4 \cdot AlCl_3$ adduct showed²¹ that $AlCl_3$ increases the bond length of the extended Te-Cl bonds resulting in greater positive charge on the $TeCl_3$ unit. It was shown by Bergman³⁷ that telluration of some aromatic compounds such as benzene, toluene, *etc.* with $TeCl_4$ is achieved only in the presence of $AlCl_3$. Similar results were obtained in our work. Reactions (1) and (2) were enhanced in the presence of $AlCl_3$ and reaction (13) took place only in the presence of $AlCl_3$.

Solvents such as diethyl ether, dioxan, pyridine, *etc.*, which co-ordinate with TeX_4 , increase its electron density and the energy of activation towards nucleophilic attack on its halide resulting in the release of TeX_2 . Nucleophilic displacement on tellurium becomes dominant under such conditions; *e.g.* in the reaction of $TeCl_4$ with styrene chlorination occurs in the absence of solvent⁵ or in chloroform,⁶ whereas in ether¹⁰ the product of telluration is obtained. The reaction of $TeCl_4$ with 1,1-diphenylethylene yielding $(Ph_2C:CH)_2TeCl_2$ [reaction (14)] was accomplished only in ethereal solution.

As an extension of this it might be expected that under appropriate conditions these compounds will act as source of nucleophilic halide.

(b) The tellurium in TeX_4 and $RTeX_3$ reacts as a Lewis acid with Lewis bases such as pyridine and its derivatives,³⁸⁻⁴⁰ derivatives of ethylenediamine,^{35,41} thiourea,^{40,42} ether,^{14,16} and X^- .^{4a}

(c) Te^{IV} compounds are reduced by reagents of low ionization potential such as metals, anions^{2,3,4b} (thio-sulphates, disulphite, sulphite, sulphide), hydrazine and its derivatives, thiourea,¹⁸ and thiosulphonates.⁴³

(d) The $(TeCl_3)^{\delta+}$ unit exhibits its electrophilic character not only by reaction at the tellurium site leading to telluration but also, alternatively, at chlorine leading to electrophilic chlorination (see later).

(e) In non-co-ordinating polar solvents the polarity of

the bond $X_3Te^{\delta+} \cdots X^{\delta-}$ is increased and the electrophilic reactivity is expected to increase.²¹ It is shown in Table I that in the chlorination of anthracene by $TeCl_4$ the reaction is enhanced in more polar solvents ($CH_2Cl_2 > CHCl_3 > PhMe \geq PhH$).

In the light of Hudson's work^{44,45} the question of whether telluration or chlorination will predominate can be considered from the point of view of perturbation MO theory with inclusion of electron-electron repulsion terms. If we assume that the positive charge on tellurium in $(TeCl_3)^{\delta+}$ is greater than that on chlorine, telluration should predominate in charge-controlled reactions (with strongly negatively charged or polar nucleophiles) whereas chlorination should predominate in orbital-controlled reactions. In addition since the tellurium atom is more hindered than the chlorine atom it is to be expected that chlorination will be favoured with increasing size of nucleophile.

The following data correlate with the above.

(i) The reactions of TeX_4 and its derivatives with olefins result mostly in chlorination, sometimes accompanied by minor amounts of telluration, and with anthracene result in chlorination only (see above).

(ii) Telluration has been found in the reactions of $TeCl_4$ and $ArTeX_3$ with polar nucleophiles^{2,3} such as anisole and its derivatives, aniline and its derivatives, phenetole, aromatic alcohols, diphenyl ether, and aromatic thioethers.^{2,3}

(iii) In the reactions of TeX_4 and $ArTeX_3$ with aromatic systems^{2,3} such as anisole, phenetole, diphenyl ether, *etc.*, *para*-substituted products are obtained, consistent with high sensitivity to steric hindrance.

(iv) Anionic nucleophiles such as halide anions^{4c} react with TeX_4 at the tellurium to give the complex ions TeX_5^- and TeX_6^{2-} .

(v) Water, aqueous bases, alcohols, and acids and their anions cause decomposition of Te^{IV} compounds by nucleophilic attack on the tellurium atom.^{3,4d}

(vi) The yields of telluration products increase in the order¹⁰ 1,1-di-*m*-xylylethylene > 1,1-di-*p*-tolylethylene > 1,1-diphenylethylene, in keeping with increase in electron density on the olefinic methylene group.

Our own results for the reactions of anthracene with TeX_4 and Ar_nTeX_{4-n} ($n = 1$ or 2 , $Ar = Ph$ or *p*-MeO-C₆H₄) indicate that the halogenated products result from nucleophilic attack of anthracene (positions 9 and 10) on the halogens of $TeX_3^{\delta+}$ or $(Ar_nTeX_{3-n})^{\delta+}$. Alternative mechanisms such as free-radical halogenation or the halogenation of anthracene by molecular chlorine are unlikely. On the one hand no anthracene dimers,⁴⁶ whose

³¹ G. D. Cristofferson, R. A. Sparks, and J. D. McCullough, *Acta Cryst.*, 1958, **11**, 782.

³² G. D. Cristofferson and J. D. McCullough, *Acta Cryst.*, 1958, **11**, 249.

³³ G. Y. Chao and J. D. McCullough, *Acta Cryst.*, 1962, **15**, 887.

³⁴ S. C. Abrahams, *Quart. Rev.*, 1956, **10**, 407.

³⁵ I. R. Beattie and H. Chudzyska, *J. Chem. Soc. (A)*, 1967, 894.

³⁶ K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, 1971, **10**, 1871.

³⁷ J. Bergman, *Tetrahedron*, 1972, **28**, 3323.

³⁸ D. A. Couch, P. S. Elmes, J. E. Fergusson, M. L. Greenfield, and C. J. Wilkins, *J. Chem. Soc. (A)*, 1967, 1813.

³⁹ I. R. Battie, M. Milne, and M. Webster, *J. Chem. Soc. (A)*, 1969, 482.

⁴⁰ N. Katsaras and J. W. George, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3503.

⁴¹ I. R. Beattie, J. R. Horder, and P. J. Jones, *J. Chem. Soc. (A)*, 1970, 329.

⁴² O. Foss, *Acta Chem. Scand.*, 1961, **15**, 1939.

⁴³ O. Foss, *Acta Chem. Scand.*, 1952, **6**, 521.

⁴⁴ G. Klopman, and R. F. Hudson, *Theor. Chim. Acta*, 1967, **8**, 165.

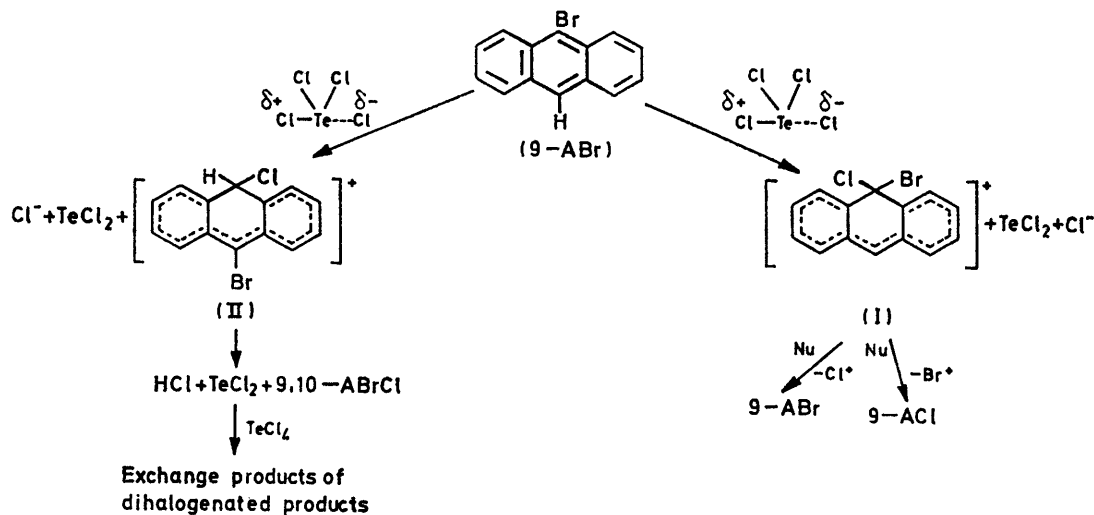
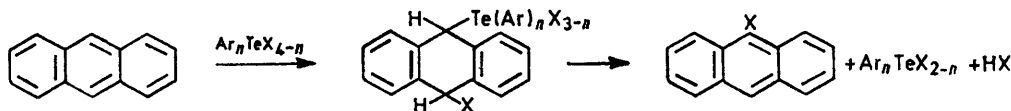
⁴⁵ R. F. Hudson, *Angew. Chem. Internat. Edn.*, 1973, **12**, 36.

⁴⁶ V. D. Parker, *Acta Chem. Scand.*, 1970, **24**, 3151.

formation during free-radical halogenation would be expected, were found, while on the other the decomposition of the TeCl_4 to $\text{TeCl}_2 + \text{Cl}_2$ does not occur below 500°C .⁴⁷ A mechanism which can explain most of the results is one involving addition-elimination (Scheme 2). The first step of such a reaction would be telluration of

A catalogue of the polyhalogenated anthracenes produced in reactions (10) and (11), and the probable halogenation and exchange halogenation pathways leading to them, is presented in Scheme 4.

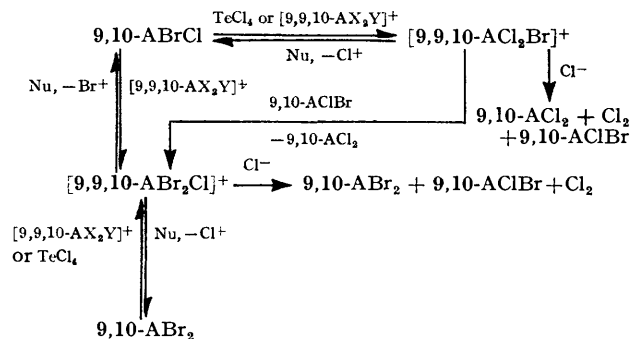
The possibility that halogen exchange is the result of reaction of halogenated anthracene with HX (catalysed



$\text{Ar}_n\text{TeX}_{3-n}$, which explains the influence of solvent and AlCl_3 as well as the relative reactivities of anthracene and halogenated anthracene, and the relative reactivities of the compounds $\text{Ar}_n\text{TeX}_{4-n}$ (above). The exchange of halogen or halogenated anthracene [reactions (9)–(11)] can be ascribed, for example for reaction (9), to the addition of TeCl_4 to 9-ABr and the elimination of TeCl_3Br . However, were such an addition-elimination mechanism operative one might expect to find telluration products, which we did not. Furthermore the 1,1-diphenylvinyl chloride obtained in reaction (14) would not be an expected product of the addition-elimination mechanism.

We therefore prefer a mechanism involving direct nucleophilic attack on the halogen of $\text{TeX}_3^{\delta+}$. Such an attack is most reasonable for the reaction of Ph_3P with TeCl_4 [reaction (15)], since Ph_3P is well known for its nucleophilic attack on 'positive' halogen.^{48,49} In the case of anthracene such a nucleophilic attack, leading to C-X σ -bond formation at position 9 (or 10) would produce a cationic intermediate of type (I) or (II), which in the case of halogenated starting materials could lead to exchange of halogen as indicated in Scheme 3, where Nu is a nucleophile, e.g. anthracene and its derivatives or Cl^- .

by TeCl_4) seems excluded by the findings for reactions (10) and (11). In these HX is not a product but Cl_2 is. The latter may of course be responsible for a part of the halogen exchange.



The intermediate (I) suggested above is in accord with the fact that 9-bromoanthracene is protonated preferentially at position 9.⁵⁰ The fact that the most abundant end-product in experiments (10) and (11) is 9,10- ACl_2 can be related to the greater strength of the C-Cl than of the

⁴⁷ J. H. Simons, *J. Amer. Chem. Soc.*, 1930, **52**, 3488.

⁴⁸ F. G. Bordwell and B. B. Jarvis, *J. Amer. Chem. Soc.*, 1973, **95**, 3583.

⁴⁹ R. Rabinowitz and R. Marcus, *J. Amer. Chem. Soc.*, 1962, **84**, 1312.

⁵⁰ G. A. Olah, 'Friedel Crafts and Related Reactions,' Interscience, New York, 1964, vol. I, p. 729.

C-Br. No chlorination was found in the reactions of anthracene with Ph_2TeCl_2 and $(p\text{-MeO}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2$. This phenomenon is also consistent with the bonding model discussed above. In compounds of this type both electronegative chlorine atoms would be expected to occupy apical positions and to carry a relatively high negative charge; neither therefore would exhibit electrophilic reactivity. Nucleophilic attack on tellurium only is found with R_2TeCl_2 (e.g. halide exchange).^{4e,10,16} In the presence of Ag^+ , however, even Ar_2TeCl_2 acts as a chlorinating agent [see reactions (5) and (6)]. This we explain by postulating the formation of $[\text{Ar}_2\text{TeCl}]^+$ (since AgCl is precipitated) and nucleophilic attack of the anthracene on the chlorine of this cation. The fact that in reaction (5) both 9- ACl and 9,10- ACl_2 were formed whereas in reaction (6) only 9- ACl was produced is worthy of note. It shows, not unexpectedly in view of the above discussion, that Ph_2TeCl_2 is a stronger chlorinating agent than $(p\text{-MeO}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2$.

The reactions of TeCl_4 with benzene in the presence of AlCl_3 and with 1,1-diphenylethylene in ether [reactions (13) and (14)] are examples of competitive nucleophilic attack on tellurium and on chlorine to give both telluration and chlorination resulting (13) in Ph_2TeCl_2 and PhCl or (14) $(\text{Ph}_2\text{C}\cdot\text{CH})_2\text{TeCl}_2$ and $\text{Ph}_2\text{C}\cdot\text{CHCl}$.

EXPERIMENTAL

N.m.r. spectra were taken with a Varian HA-100 spectrometer with Me_4Si as internal standard. Mass spectra were taken with a Hitachi-Perkin-Elmer RMU6 spectrometer at 70 eV. I.r. spectra were taken with a Perkin-Elmer 257 grating spectrometer. Gas chromatographic identifications were made with a Packard G.C. 824 instrument (flame ionization detector) [columns (2 m \times 2 mm i.d.) filled with 3% OV1 or 3% SE30 on GasChrom Cl]. Preparative separations were carried out on a Varian Aerograph 920 instrument [1.5% OV101 on GasChrom Q (2 m \times 3/8 in. i.d.)]. M.p.s taken with a Unimelt Thomas-Hoover apparatus.

Materials.— TeCl_4 , TeBr_4 , and TeI_4 were of analytical grade (Alpha Inorganics Ventron) and were used without further treatment. Recrystallization of the tellurium reagents before use was found to be ineffective. Elemental tellurium was of 99.99% purity (Merck). Anthracene was of C.P. grade (Fluka A.G.); it was co-distilled with ethylene glycol⁵¹ and twice recrystallized from ethanol. 1,1-Diphenylethylene was synthesized according to Allen.⁵² All solvents were of analytical grade (Frutarom, Haifa) and were purified according to directions given by Perrin.⁵¹ Solvents were stored after purification over 3 Å molecular sieves.

Reactions.—All the reactions were carried out by using variations of the same basic procedure. The tellurium compounds and the organic substrates were mixed and stirred under nitrogen. The exchange reactions of anthracene [reactions (9)—(11)] were carried out in refluxing CH_2Cl_2 and the molar ratios of TeCl_4 to 9- ABr , 9,10- ABrCl , and 9,10- ABr_2 were 3 : 1. In the reaction of 1,1-diphenylethylene the molar ratio of 1,1-diphenylethylene to TeCl_4 was 1.5 : 1; the directions given by Patai *et al.*¹⁰ were followed.

⁵¹ D. D. Perrin, W. L. F. Ararego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, Oxford, 1966, ch. 3.

⁵² C. F. H. Allen and S. Converse, *Org. Synth.*, 1941, 1, 226.

⁵³ D. Elmaleh, personal communication (see ref. 10).

In all the other reactions the molar ratio of the reactants was 1 : 1. In the reaction with 1,1-diphenylethylene only a small part of the TeCl_4 should be used to start the reaction, with the rest added after the red colour has appeared.⁵³

Products.—9,10-Dichloroanthracene, 9-chloroanthracene, 9,10-dibromoanthracene, and 9-bromoanthracene were separated and identified by means of n.m.r. and mass spectra and by mixed m.p. determinations with authentic samples synthesized by the procedure of Ware and Borchert.⁵⁴

9-Bromo-10-chloroanthracene was separated quantitatively by g.l.c. (m.p. 209°). This compound was synthesized by refluxing 9-chloroanthracene with CuBr_2 (molar ratio 1 : 2) for 10 h in CCl_4 . The mixture was treated with water and the product was separated by g.l.c. from the dried (MgSO_4) organic layer. The mass spectrum showed m/e 290 (M^+) 292 ($M + 2$), 294 ($M + 4$), 255 and 257 ($M - \text{Cl}$), 211 and 213 ($M - \text{Br}$), and 176 [$M - (\text{Cl} + \text{Br})$]. The n.m.r. spectrum showed the pattern typical of a 9,10-dihalogenoanthracene.

$p\text{-MeO}\cdot\text{C}_6\text{H}_4\text{TeCl}_3$ was synthesized according to Morgan⁵⁵ and crystallized from acetonitrile.

$(p\text{-MeO}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2$ was identified by its m.p. (180—182°; lit.,⁴⁵ 182°) and by mixed m.p. with an authentic³⁷ sample; δ (CDCl_3) 3.83 (3H, s), 6.98 (2H, d, J 9 Hz), and 7.95 (2H, d, J 9 Hz); m/e 371—381 ($M - \text{Cl}$) and 336—344 ($M - 2\text{Cl}$).

Ph_2TeCl_2 was synthesized according to Reinholdt.²

$(p\text{-MeO}\cdot\text{C}_6\text{H}_4)_2\text{Te}$ was formed by treating $(p\text{-MeO}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2$ with anthracene in refluxing ethyl methyl ketone for 18 h in the presence of AgNO_3 . It was separated by recrystallization of the resulting solid mixture from ethanol and identified by its m.p. (55—56°; lit.,³⁷ 56—57°) and mixed m.p. with an authentic sample.³⁷ Its n.m.r. spectrum was identical with that reported.³⁷ Characteristic mass-spectral peaks appeared at m/e 336—344 (M^+).

Dichlorobis-(2,2-diphenylvinyl)tellurium precipitated during the reaction of $\text{Ph}_2\text{C}\cdot\text{CH}_2$ with TeCl_4 . It was filtered off, washed with ethanol, and recrystallized from ethanol or CCl_4 to give white needles which turned pink in light; m.p. 241—242°; δ (CDCl_3) 7.36 (10H, s), 7.45 (10H, s), and 7.99 (2H, s); m/e 523 ($M - \text{Cl}$) and 480—488 ($M - 2\text{Cl}$) (Found: C, 60.1; H, 3.95; Cl, 12.6; Te, 23.1. $\text{C}_{28}\text{H}_{22}\text{Cl}_2\text{Te}$ requires C, 60.35; H, 3.95; Cl, 12.6; Te, 23.1%).

Reaction of triphenylphosphine with tellurium tetrachloride. TeCl_4 was refluxed under nitrogen for 4 h with Ph_3P in benzene. The mixture was filtered and the filtrate washed with aqueous 10% sodium hydrogen carbonate and then water to neutrality. It was dried (CaCl_2) and evaporated under reduced pressure. The solid residue was crystallized from n-hexane. Ph_3PO , identified by m.p. (155°; lit.,⁵⁶ 156°) and mixed m.p. with an authentic sample, showed ν_{max} 1180 cm^{-1} ($\text{P}=\text{O}$);⁵⁶ m/e 278 (M^+).

The inorganic residue. The inorganic residue from all the reactions of TeX_4 cited was purified by Soxhlet extraction of the organic materials with CCl_4 and dried under vacuum. Analysis for Te and Cl or Br showed a higher proportion of Te than expected for TeCl_2 or TeBr_2 (no C or H was found). From the reaction of $p\text{-MeO}\cdot\text{C}_6\text{H}_4\text{TeCl}_3$ and anthracene only elemental tellurium and $(p\text{-MeO}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2$ (1:1) were isolated. No $p\text{-MeO}\cdot\text{C}_6\text{H}_4\text{TeCl}$ was found.

Tellurium and its dichloride. TeCl_2 was identified by its disproportionation reaction to TeCl_4 and Te on refluxing in

⁵⁴ J. C. Ware and E. E. Borchert, *J. Org. Chem.*, 1961, 26, 2263.

⁵⁵ G. T. Morgan and R. E. Kellett, *J. Chem. Soc.*, 1926, 1080.

⁵⁶ J. C. Sheldon, *J. Amer. Chem. Soc.*, 1958, 80, 2117.

ether and the precipitation of the TeCl_4 formed as its pyridine complex. The mass spectrum of the residue ($\text{Te} + \text{TeCl}_2$) showed the characteristic peaks at m/e 192—204 (TeCl_2^{++}), 156—167 (TeCl^+), 244—260 (Te_2^{++}), and 122—130 (Te^+). In the case of $\text{TeBr}_2 + \text{Te}$ the peaks were at m/e 280—292 (TeBr_2^{++}), 201—211 (TeBr^+), 244—260 (Te_2^{++}), and 122—130 (Te^+). Peaks at m/e 244—260 and 122—130 are found in the mass spectrum of elemental tellurium.

Solvent Adducts of Tellurium Tetrachloride.—The TeCl_4 -solvent adducts were obtained by stirring 0.01M- TeCl_4 in

ether or dioxan (15 ml) under reflux for 15 h and then cooling the mixture in ice-cold water. The crystals were filtered off in a glove bag and dried under vacuum for 2 h. The crystals of the TeCl_4 -dioxan adduct were yellowish plates showing a typical n.m.r. spectrum for dioxan shifted to low field by 12 Hz. The TeCl_4 -ether adduct formed golden-yellow needles showing a typical n.m.r. spectrum for ether shifted to low field by 2 Hz for the methyl signal and 5 Hz for the methylene signal.

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