PRESIDENTIAL ADDRESS.

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Recent Researches on Certain of the Rarer Elements.

FOR the last five years, Presidential Addresses to the Chemical Society have been devoted wholly or in part to considerations affecting the professional and scientific activities of British chemists, and it is undoubtedly the fact that ideas of federation and co-operation have for some time past been stirring in the minds of many members both of this Society and of kindred associations. Discussions have now been in progress for more than two years between representatives of the three Chartered bodies, the Chemical Society, the Institute of Chemistry, and the Society of Chemical Industry. An agreed scheme of co-operation drafted in legal form has now been published and circulated to all members of these three bodies. If this document receives the final approval of the Councils concerned it will mark the first step towards a federal reunion of the institutions representing chemical science in this country.

The Provisional Council, which under the able and zealous Chairmanship of Mr. J. Davidson Pratt has conducted these negotiations, has every confidence that its draft scheme will meet with general approval and if this anticipation is realised it is highly probable that other chemical associations may wish to participate. If such accessions are realised the movement for federation will acquire still greater impetus. As, however, the matter is now before the chemical public, I do not propose to ventilate it further this afternoon but to employ the short time at my disposal in discussing a purely chemical topic.

Organic Derivatives of Selenium and Tellurium.

Fifteen years ago it was known that acetylacetone, the most frequently studied of the β-diketones, furnished with a majority of the chemical elements derivatives which could be classified into three main groups :—

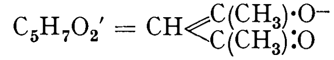
I. Metallic acetylacetones in which the principal valencies of the metal are satisfied completely by a univalent radical $C_5H_7O_2'$. To this group belong the acetylacetones of aluminium, beryllium, chromium, copper, iron, scandium, thorium, zinc, and numerous others.

II. Acetylacetones of the non-metals, metalloids and metals in which the principal valencies of these elements are only partly satisfied by the univalent radical. Such are the compounds of boron, silicon, and titanium, which function as ionised chlorides, giving rise to complex double salts (Dilthey, 1905). To this group also belong certain complex acetylacetones, for instance, those of platinum, $[2C_5H_7O_2' \, Pt^{II} \, Cl]M$, where M = H, Na, K, or Rb (Werner, 1901), and of cobalt $[C_5H_7O_2' \, Co, 2en]X_2$, where X = Cl, Br, or I (Werner, 1918).

III. Acetylacetones of sulphur which are true organic derivatives of this element containing the non-metal in direct attachment with carbon and not through the intervention of oxygen as in the preceding groups (Angeli and Magnani, Negri, 1893; Vaillant, 1894). Such sulphur derivatives would probably repay further study.

Subsequent researches in the Birmingham University laboratories added gallium to the first group (1921), germanium and zirconium to the second group (1924), and selenium to the third (1922). The late Dr. T. V. Barker, who participated in the last-mentioned research, showed that the selenium derivative was isomorphous with the corresponding sulphur compound.

Acetylacetone Derivatives.



$$C_5H_7O_2' = CH\begin{matrix}\diagup C(CH_3)\cdot O- \\ \diagdown C(CH_3):O\end{matrix}$$

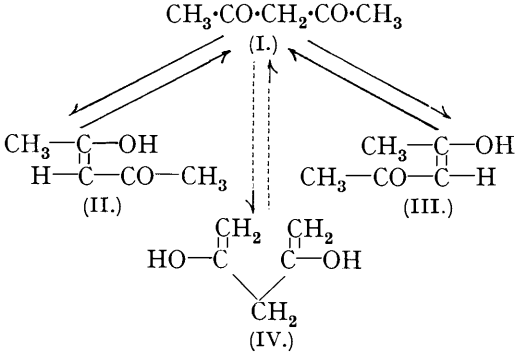
$Tl^I\cdot C_5H_7O_2$ $Be(C_5H_7O_2)_2$ $Al(C_5H_7O_2)_3$ $Sc(C_5H_7O_2)_3$ $Cr(C_5H_7O_2)_3$ $Th(C_5H_7O_2)_4$	$[B(C_5H_7O_2)_2]Cl$ $[Si(C_5H_7O_2)_3]Cl$ $[Ti(C_5H_7O_2)_3]Cl$ $[Ge(C_5H_7O_2)_2Cl_2]$ $[Ge(C_5H_7O_2)_3]Cu^ICl_2$ (1924.)	$S(C_5H_7O_2)_2$ $S_2(C_5H_7O_2)_2$ $S_3(C_5H_7O_2)_2$
$Ga(C_5H_7O_2)_3$ (1921.)	$[Zr(C_5H_7O_2)_3]Cl$ (1924.)	$Se_2(C_5H_7O_2)_2$ (1922.)
(I.)	(II.)	(III.)

Although the members of these three groups of acetylacetone derivatives differ considerably in type, they possess one attribute in common. They contain the same univalent radical $C_5H_7O_2'$, of which one or more are present in all the acetylacetone derivatives examined up to 1920.

In that year, Dr. Drew and I began a study of the interactions between acetylacetone and the tetrachlorides of selenium and tellurium. Our preliminary experiments showed that the main products differed from all previously known acetylacetone derivatives in containing a bivalent radical $C_5H_6O_2''$, and although fourteen years have elapsed selenium and tellurium still remain the only two elements which are known to give this result. I propose in the first place to summarise the advance in chemical knowledge which has accrued from these observations.

Acetylacetone.

Isomeric and Tautomeric Forms.



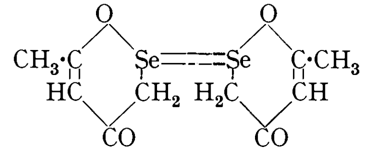
Acetylacetone is commonly known as an equilibrium mixture of the diketone (I) with its monoenolic modification, the latter probably existing in two stereoisomeric forms (II and III). The acetylacetone derivatives known up to 1920 are all derived from the *trans*-monoenolic form of this β-diketone, so that when the hydroxylic hydrogen is replaced by a metal or metalloid the remaining organic residue furnishes a five-membered chelate group which implicates the metallic or metalloidal atom in a six-membered ring.

I now propose to show first that the other *cis*-monoenolic form is operative in the condensations with selenium tetrachloride and secondly that a fourth tautomeric modification is revealed in the condensations with tellurium tetrachloride. It will be obvious that there are several other tautomeric forms of the β-diketone possible between the limits of two-fold terminal enolisation and either of the monoenolic forms. In these intermediate phases, enolisation will be partly terminal and partly median. Evidence of the intervention of such intermediate forms will also be disclosed in the tellurium tetrachloride condensations. Actually the experimental demonstration of these new modes of β-diketone interaction was the work of many investigators spread over several years, for at the outset it was supposed that the organic bivalent radical $C_5H_6O_2''$ involved was the same in both cases.

Acetylacetone with Tetrachlorides of Selenium and Tellurium.

(Early interpretation of the selenium and tellurium reactions.)

$$2SeCl_4 + 4C_5H_8O_2 = [C_5H_6O_2{:}Se]_2 + 2C_5H_7ClO_2 + 6HCl$$

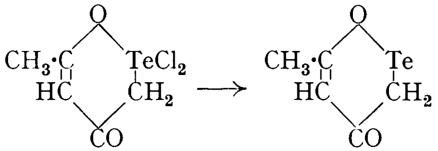


$$[C_5H_6O_2{:}Se]_2 + 4RHSO_3 = 2C_5H_8O_2 + 2Se(SO_3R)_2$$

$$R = H, Li, Na, K, Rb, Cs, [NH_4], \text{ or } Ba_{\frac{1}{2}}$$

$$TeCl_4 + C_5H_8O_2 = C_5H_6O_2{:}TeCl_2 + 2HCl$$

$$C_5H_6O_2{:}TeCl_2 + H_2SO_3 + H_2O = C_5H_6O_2{:}Te + H_2SO_4 + 2HCl$$



The above scheme indicates the observed condensations. In the reaction with selenium tetrachloride the selenium parted with all its chlorine and yielded a dimeric product containing two molecular proportions of the bivalent radical combined with two atomic proportions of selenium; the other products were 3-chloroacetylacetone and hydrogen chloride.

A practical outcome of this part of the work was soon noticed. This selenium acetylacetone was reduced quantitatively by sulphurous acid or aqueous bisulphites. Acetylacetone was regenerated and selenodithionic acid or its salts were obtained free from other seleniferous products. These salts were obtained crystalline; the free acid was concentrated to a 50% aqueous solution.

The main reaction with tellurium tetrachloride led to tellurium acetylacetone dichloride, reduced by sulphurous acid or aqueous bisulphite to yellow tellurium acetylacetone.

Our first deductions from these experiments were that in each case we were dealing with the same bivalent radical. Later experiments compelled us to abandon the formulations expressing this view. It will be convenient to take the selenium derivatives first.

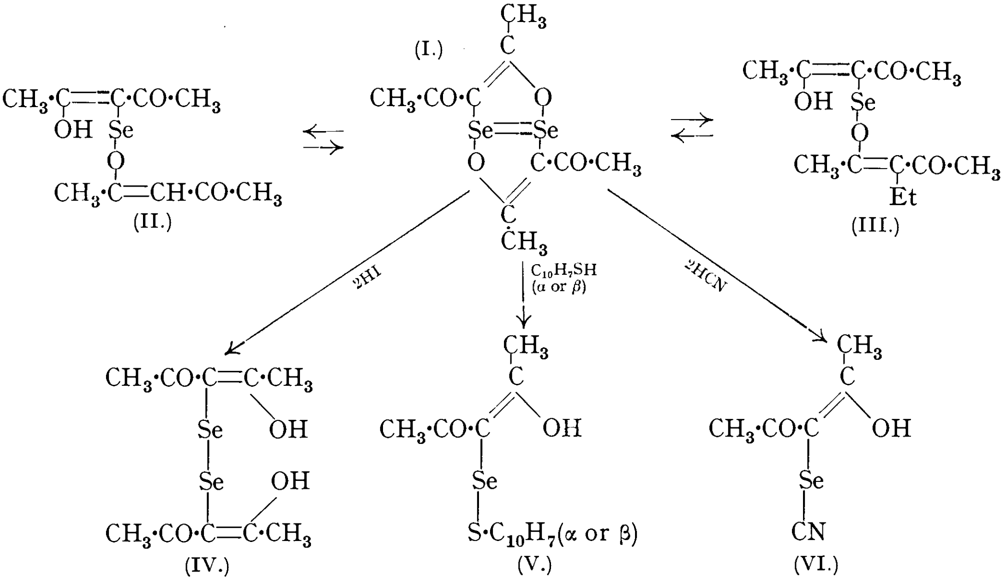
Selenium Derivatives of β-Diketones.

The large proportion of hydrogen chloride set free in the selenium tetrachloride reaction exerts a destructive action on the seleniferous product and it was found desirable to diminish this acidity by employing copper acetylacetone rather than the β-diketone itself.

The dimeric selenium acetylacetone (I) contains no enolic group but it reacts with excess of acetylacetone to give rise to selenium *OC*-bisacetylacetone (II), which is mono-enolic as shown by the formation of a copper derivative.

The dimeric compound also reacts with *C*-ethylacetylacetone, hydriodic acid, hydrogen cyanide, and the thionaphthols as shown in the following diagram.

Reactions of Selenium Acetylacetone.



The first reagent gives selenium *C*-ethyl-*OC*-bisacetylacetone (III). The reaction with hydriodic acid goes to completion and the iodine liberated may be estimated quantitatively. The product, diselenium bisacetylacetone (IV), an orange-coloured dienolic compound, may also be prepared by condensing selenium monochloride, Se_2Cl_2, with copper acetylacetone.

With hydrogen cyanide the opening of the ring in selenium acetylacetone proceeds smoothly with formation of a monoenolic selenocyanate (VI), whereas with the thionaphthols monoenolic thio-ethers (V) are produced.

All these chemical changes support the view that in the dimeric selenium acetylacetone (I), selenium replaces one hydrogen from the enolic radical and one from its attachment to the central carbon atom. The resulting bivalent radical, $C_5H_6O_2''$, is derived from the *cis*-monoenolic form of the β-diketone.

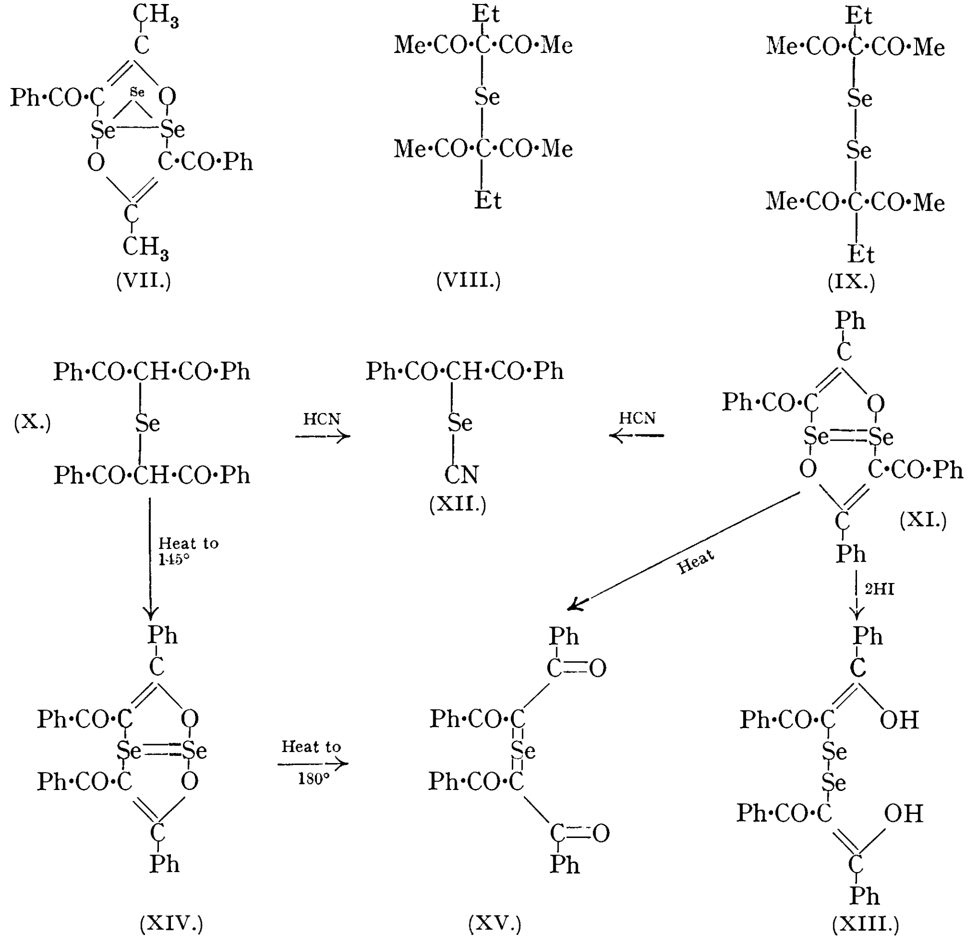
This condensation was extended to other β-diketones such as acetylpropionylmethane, ω-phenylacetylacetone, β-phenylpropionymethane, and benzoylacetone. It was then found that these homologues of acetylacetone, which still contain an unsubstituted methylene residue, all give rise to dimeric selenium derivatives similar in constitution to selenium acetylacetone (I). The condensation with benzoylacetone was noteworthy, since it also led to the compound (VII) which contains three selenium atoms.

The condensations with selenium tetrachloride proceed otherwise when one hydrogen of the methylene group is replaced by an alkyl radical. When the copper derivative of *C*-ethylacetylacetone reacts with selenium tetrachloride, only one hydrogen is displaced from each molecule of the β-diketone. Two products are formed (VIII and IX); they contain respectively one and two atomic proportions of selenium depending on the amount of selenium tetrachloride employed. Both products are non-enolic.

As a final and significant example of these condensations the case of dibenzoylmethane may be cited. The general chemistry of this β-diketone indicates that it enolises somewhat sluggishly. If one of the methylene hydrogens is replaced by halogen, the product is non-enolic. With selenium tetrachloride, two primary products are obtained. One contains two univalent groups attached to one selenium atom (X); the other is a dimeric substance (XI) containing two bivalent radicals, each of which is formed by elimination of two hydrogen atoms originally derived from the methylene group. Hydrogen cyanide reacts with each of these primary products, forming a selenocyanate (XII) which in this case is non-enolic. Hydriodic acid and the dimeric compound yield a dienolic diselenide (XIII) with liberation of iodine.

Selenium Derivatives of β-Diketones.

(Benzoylacetone, *C*-ethylacetylacetone, and dibenzoylmethane.)



(VII.) (VIII.) (IX.) (X.) (XII.) (XI.) (XIV.) (XV.) (XIII.)

The remaining reactions shown in the diagram were observed only in the case of dibenzoylmethane. On heating gently, the monoselenium compound (X) loses dibenzoylmethane and gives rise to a dimeric substance (XIV) isomeric with the normal one (XI). At higher temperatures this isomeride sheds half its selenium and passes into a compound containing one atomic proportion of selenium associated with two bivalent groups. This orange-coloured dehydrobisbenzoylmethane (XV) is not attacked by hydriodic acid, but when reduced with sodium amalgam in aqueous alcohol it yields dibenzoylmethane, acetophenone, and benzoic acid with elimination of selenium. This reduction throws some light on its constitution.

These experimental results all point to the same conclusion that in reactions between β-diketones or their copper derivatives and selenium tetrachloride the attack of the latter is directed entirely towards the median methylene group so that a bivalent radical is manifested only when, in addition to one enolic hydrogen or its copper equivalent, there is present another hydrogen atom attached directly to the median carbon of the β-diketone. When these two conditions are satisfied, a dicyclic system is established as shown in the revised formulations for all the dimeric selenium derivatives of the series.

Tellurium Derivatives of β-Diketones.

I shall now endeavour to show how in its interactions with β-diketones, tellurium tetrachloride induces a development of the tautomeric forms of these organic reagents. With acetylacetone itself the condensation was effected in ordinary chloroform and under these conditions there were three products. The main product was tellurium acetylacetone dichloride, a compound containing the bivalent radical $C_5H_6O_2''$ combined with a $TeCl_2$ residue. In addition there were two by-products, the first an enolic compound which retains the property of giving characteristic ferric and cupric derivatives; the second a singular ethyl ether which arises from the circumstance that chloroform B.P. contains ethyl alcohol. These two by-products suggest the intervention of those tautomeric forms of the β-diketone in which enolisation is partly terminal and partly median. With the ascent of the homologous series of β-diketones a fourth type of by-product appears, as in the condensations with dibutyrylmethane, *n*-heptoylacetone and *n*-nonoylacetone. These homologues of acetylacetone furnish tellurium trichlorides of which the product from *n*-heptoylacetone may be formulated as indicated in the above diagram.

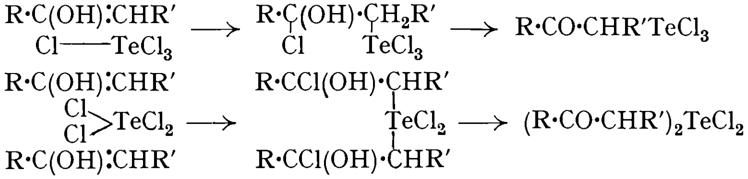
Non-cyclic Tellurium Derivatives of Mono- and β-Di-ketones containing Univalent Radicals.

I. From Acetylacetone and Homologues

$\{CH_3{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH_2\}_2TeCl_2$ (enolic)
$CH_3{\cdot}C(OC_2H_5){:}CH{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$ (*O*-ether)
$C_6H_{13}{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CH_2{\cdot}TeCl_3$ or
$C_6H_{13}{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$ (enolic)

II. From Mono-ketones

$(CH_3{\cdot}CO{\cdot}CH_2)_2TeCl_2$ $C_2H_5{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$
$(CH_3)_3C{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$ and $\{(CH_3)_3C{\cdot}CO{\cdot}CH_2\}_2TeCl_2$



$$\begin{array}{c}R{\cdot}C(OH){:}CHR'\\ Cl\text{——}TeCl_3\end{array} \longrightarrow \begin{array}{c}R{\cdot}\overset{|}{C}(OH){\cdot}\overset{|}{C}H_2R'\\ Cl\quad TeCl_3\end{array} \longrightarrow R{\cdot}CO{\cdot}CHR'TeCl_3$$

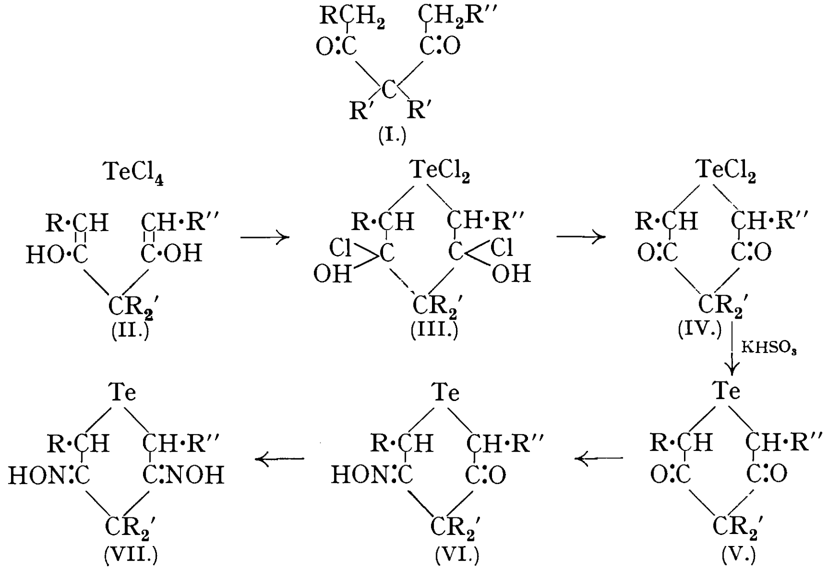
$$\begin{array}{c}R{\cdot}C(OH){:}CHR'\\ {}^{Cl}_{Cl}{>}TeCl_2\\ R{\cdot}C(OH){:}CHR'\end{array} \longrightarrow \begin{array}{c}R{\cdot}CCl(OH){\cdot}CHR'\\ TeCl_2\\ R{\cdot}CCl(OH){\cdot}CHR'\end{array} \longrightarrow (R{\cdot}CO{\cdot}CHR')_2TeCl_2$$

At this stage, reference may appropriately be made to a joint study with Mr. O. C. Elvins on the interaction of tellurium tetrachloride and simple ketones. Contrary to the statement of Michaelis's pupil, Rust, acetone does react with the tetrachloride and gives tellurium bisacetone dichloride, $(CH_3{\cdot}CO{\cdot}CH_2)_2TeCl_2$. The next homologue, methyl ethyl ketone, yields a trichloride, $C_2H_5{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$. Pinacolin (methyl *tert.*-butyl ketone) is of special interest, for it furnishes both types of tellurium derivative, $(CH_3)_3C{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$ and $\{(CH_3)_3C{\cdot}CO{\cdot}CH_2\}_2TeCl_2$. With increasing substitution of alkyl groups for hydrogen the property of reacting with tellurium tetrachloride gradually disappears. Di*iso*propyl ketone is quite unaffected by this reagent. The two modes of reaction may be generalised as shown in the above diagram.

It is noteworthy that these derivatives of the monoketones containing quadrivalent tellurium are colourless even when R is an aryl group.

One may apply similar reasoning to the interactions of tellurium tetrachloride and β-diketones, of which many examples have been studied. The general formula for any β-diketone which will react with tellurium tetrachloride to form a cyclic compound containing a bivalent chelate group is shown in (I) (following diagram). Under the influence of the tetrachloride the diketone assumes a terminal dienolic form. Addition of the tetrachloride then takes place to give the additive compound (III), separating as an oil from benzene solution, from which hydrogen chloride is eliminated with recovery in the cyclic compound (IV) of the diketo-form.

Cyclic Tellurium Derivatives of β-Diketones.



The cyclic dichloride is readily reduced by aqueous alkali bisulphite to give the corresponding *cyclo*telluropentanedione. This is a truly organometalloidal derivative containing bivalent tellurium associated on both sides with carbon and forming part of a heterocyclic six-membered ring. The existence of the two keto-groups in this ring was demonstrated by formation of oximes. Certain of these *cyclo*telluropentanediones yield monoximes (VI), others give dioximes (VII), and some give a mixture of both mono- and di-oximes. This explanation of the mechanism of the formation of the *cyclo*telluropentane ring is supported by the following facts.

1. *Median enolisation.* As long as 2R′ in the general formula (I) represents two hydrogen atoms there is considerable tendency for median enolisation to occur. With acetylacetone it leads to the two non-cyclic products already mentioned. Similar non-cyclic products have also been noticed with propionylacetone, dipropionylmethane, di-*n*-butyrylmethane and heptoylacetone. The last three diketones each exhibited the interesting case of an enolic non-cyclic trichloride (diagram on p. 559).

2. *Alkylation of the median methylene group.* When one R′ is hydrogen and the other an alkyl group, the tellurium tetrachloride condensation becomes simplified so that, although many 3-alkylated β-diketones have been examined, only one telluriferous product has been identified in each case. The case of a branched chain on the median carbon atom is noteworthy. 3-*iso*Propylacetylacetone and 3-*iso*propylpropionylacetone differ from their *n*-propyl isomerides in yielding neither ferric nor cupric derivatives, thus suggesting that an *iso*propyl group may inhibit median enolisation. Nevertheless both these diketones give *cyclo*telluripentanedione dichlorides.

When both R′ are alkyl groups as in the 3 : 3′-dialkylated β-diketones, median enolisation is entirely prevented. Nevertheless 3 : 3-dimethyl- and 3 : 3-diethyl-acetylacetones condense very smoothly with tellurium tetrachloride, giving rise solely to the *cyclo*telluripentanedione dichlorides. 3-Benzyl- and 3 : 3-dibenzyl-acetylacetones behave similarly and each yields only the one *cyclo*telluripentanedione derivative.

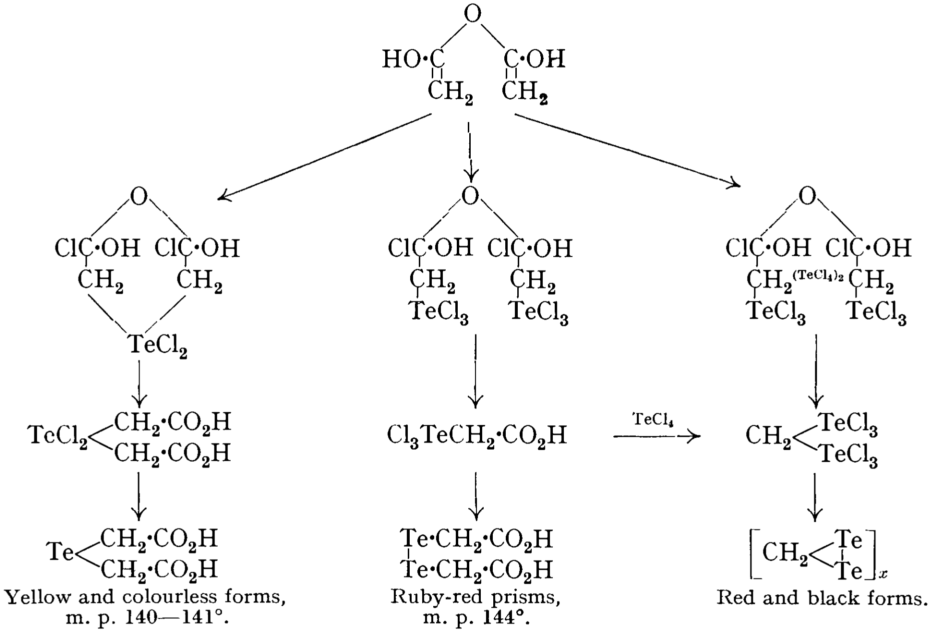
3. *Lengthening of the terminal chain.* So long as the tendency to terminal enolisation is not diminished by alkylation of the terminal methylene group, the lengthening of the hydrocarbon chain R or R″ does not prevent the formation of a *cyclo*telluripentanedione dichloride. This process has been established step by step from acetylacetone to *n*-duodecoylacetone (lauroylacetone).

Both terminal methylene groups must, however, be present. If one is converted into

CHRR′, the corresponding β-diketones yield only non-cyclic telluriferous products. The simplest case of a β-diketone with branched chains at both ends was demonstrated with di*iso*butyrylmethane, which was specially prepared for this purpose by Mr. C. J. A. Taylor. In chloroform B.P. this diketone behaved mainly as a reducing agent; nine-tenths of the tellurium present was set free and a very small amount was isolated of a tellurium *O*-ether, $CHMe_2\cdot C(OEt){:}CH\cdot CO\cdot CMe_2\cdot TeCl_3$. The influence of aromatic groups is noteworthy. A phenyl group on the median carbon atom as in 3-phenylpropionylacetone inhibits the formation of a tellurium derivative and furnishes an exception to the general rule. A phenyl group at the end of the chain as in benzoylacetone prevents any cyclic condensation; the two products are tellurium bisbenzoylacetone dichloride, $\{Ph\cdot CO\cdot CH{:}C(OH)\cdot CH_2\}_2TeCl_2$, and the *O*-ethyl derivative, $Ph\cdot CO\cdot CH{:}C(OEt)\cdot CH_2\cdot TeCl_3$.

I may now sum up the main conclusion of this long series of investigations by saying that the tellurium compounds containing bivalent radicals derived from β-diketones are truly organometalloidal substances containing tellurium implicated in a six-membered heterocyclic ring. The two hydrogen atoms eliminated in producing these bivalent radicals are derived from the enolic groups formed by two-fold terminal enolisation (formula II, p. 560). The primary products contain quadrivalent tellurium and are *cyclo*telluripentane-3 : 5-dione 1 : 1-dichlorides, which are readily reduced by aqueous bisulphites to *cyclo*telluropentane-3 : 5-diones. The latter are yellow substances sparingly soluble in water. In aqueous solution they are powerful germicides and the most potent member of the series, 2 : 6-dimethyl*cyclo*telluropentane-3 : 5-dione, is active against coliform organisms in concentrations of one in 40,000,000. Unfortunately these tellurium compounds are somewhat poisonous and induce hæmaturia. Moreover their bactericidal potency is greatly diminished in serum, probably owing to their adsorption by the small amount of fatty material present in this fluid. These bacteriological and physiological properties have been studied in detail by Dr. E. A. Cooper and several colleagues.

Tellurium Tetrachloride and Acetic Anhydride.



A logical extension of the work on β-diketones led to a study by Dr. Drew and myself of the interactions of tellurium tetrachloride and acetic anhydride. The former research showed that the formation of cyclic compounds was not affected by preventing median enolisation, as, for instance, by two-fold alkylation of the median carbon atom. This inhibition made no difference, since the attack of tellurium tetrachloride was directed towards the terminal carbon atoms. Accordingly it seemed likely that interaction would persist even if the methylene group were replaced by a single atom such as oxygen. This anticipation was confirmed in a remarkable manner by the condensations occurring between acetic anhydride and tellurium tetrachloride.

The observed chemical changes involved the reaction of acetic anhydride with one, two, or four molecular proportions of tellurium tetrachloride. After hydrolysis, the primary products were respectively dichlorotelluridiacetic acid, trichlorotelluriacetic acid and an oxygen-free methylenebistelluritrichloride. These compounds containing quadrivalent tellurium were reduced by alkali bisulphite and gave rise to tellurodiacetic acid, ditellurodiacetic acid and ditelluromethane. The first compound, a monotellurium derivative, occurs in a colourless and a yellow form. The second and third substances, containing two bivalent tellurium atoms in the molecule, are highly coloured. This association of the group –Te·Te– with a development of colour will appear in another series of tellurium derivatives containing aryl radicals.

Ditelluromethane contains nearly 95% of tellurium, but it is not merely this element contaminated with a little carbonaceous matter. It has definite molecular structure, for by addition of chlorine the hexachloride is regenerated, whereas combination with bromine leads to a yellow hexabromide.

Cyclic Tellurohydrocarbons.

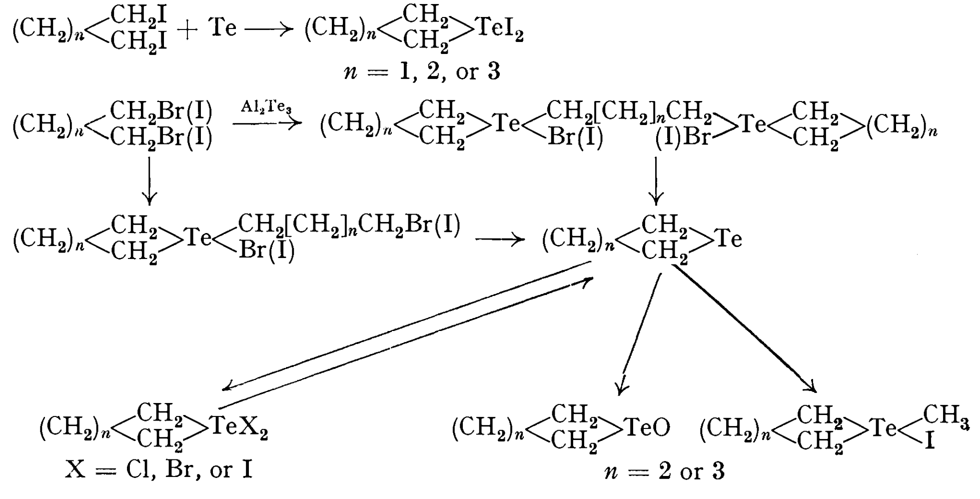
Systematic study of the main products of the interactions of tellurium tetrachloride and the β-diketones has established the existence of ring systems containing one tellurium atom and five carbon atoms. Two of these carbon atoms were oxygenated so that the cyclic compounds were diketones (p. 560).

In collaboration with Mr. F. H. Burstall and with the late Dr. H. Burgess, search was now made for the corresponding *cyclo*tellurohydrocarbons.

The following general methods were devised for the preparation of these cyclic tellurium derivatives: (1) direct combination of finely divided tellurium with alkylene di-iodides; (2) action of alkylene dihalides on aluminium telluride; and (3) interaction in alcoholic medium of alkylene dihalides and sodium telluride.

cyclo*Telluripropane* 1 : 1-*Di-iodide*.—This substance, containing a four-membered ring, was obtained by direct addition of tellurium to trimethylene di-iodide; it is not, however, readily reduced to *cyclo*telluropropane.

I. Small rings.



$$(CH_2)_n{<}\begin{smallmatrix}CH_2I\\CH_2I\end{smallmatrix} + Te \longrightarrow (CH_2)_n{<}\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}{>}TeI_2$$

$n = 1, 2,$ or 3

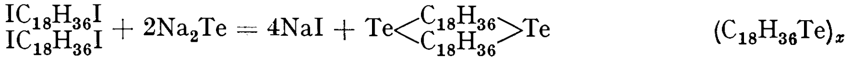
$$(CH_2)_n{<}\begin{smallmatrix}CH_2Br(I)\\CH_2Br(I)\end{smallmatrix} \xrightarrow{Al_2Te_3} (CH_2)_n{<}\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}{>}Te{<}\begin{smallmatrix}CH_2[CH_2]_nCH_2\\Br(I)\qquad(I)Br\end{smallmatrix}{>}Te{<}\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}{>}(CH_2)_n$$

$$(CH_2)_n{<}\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}{>}Te{<}\begin{smallmatrix}CH_2[CH_2]_nCH_2Br(I)\\Br(I)\end{smallmatrix} \longrightarrow (CH_2)_n{<}\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}{>}Te$$

$$(CH_2)_n{<}\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}{>}TeX_2 \qquad (CH_2)_n{<}\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}{>}TeO \qquad (CH_2)_n{<}\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}{>}Te{<}\begin{smallmatrix}CH_3\\I\end{smallmatrix}$$

$X =$ Cl, Br, or I $\qquad n = 2$ or 3

II. Large Rings.



$$\begin{smallmatrix}IC_{18}H_{36}I\\IC_{18}H_{36}I\end{smallmatrix} + 2Na_2Te = 4NaI + Te{<}\begin{smallmatrix}C_{18}H_{36}\\C_{18}H_{36}\end{smallmatrix}{>}Te \qquad (C_{18}H_{36}Te)_x$$

cyclo*Tellurobutane and* cyclo*Telluropentane.*—The five-membered ring system was established through the first general method by heating 1 : 4-tetramethylene di-iodide with tellurium; dark red, crystalline *cyclo*telluributane 1 : 1-di-iodide was then obtained in quantitative yield. Reduction with sulphurous acid led to *cyclo*tellurobutane, obtained as a light yellowish oil with nauseating odour.

The second general method with aluminium telluride was used for both five- and six-membered rings. With this process the *cyclo*tellurohydrocarbon is not isolated in one stage, since it combines additively with more of the alkylene dihalide to yield in each case two complex telluronium salts.

When heated under reduced pressure, these salts dissociate, regenerating the alkylene dihalide and liberating the *cyclo*tellurohydrocarbon, which is converted into its dibromide. This addition product is reduced with alkali metabisulphite to the tellurohydrocarbon, which is extracted with chloroform and distilled subsequently in an inert atmosphere, since it is readily oxidised to a tellurioxide. Its unsaturated character is shown by its combination with methyl iodide.

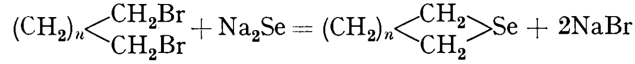
This study of *cyclo*tellurohydrocarbons indicated that, although the five- and six-membered rings could be prepared with facility, there was but little tendency for the formation of four- or seven-membered rings. As we shall notice later, this preference for five- and six-membered rings is also present among the *cyclo*selenohydrocarbons.

Since, however, the extensive researches of Ruzicka and collaborators during the last ten years have increased our knowledge of large rings with 16 to 30 members, it seemed desirable to ascertain whether it might be possible to include tellurium and also selenium in rings of this order of complexity. The interaction of sodium telluride and 1 : 18-di-iodo-octadecane in alcoholic solution under an inert atmosphere gives rise mainly to a mixture of polymerides of considerable and unknown complexity, but the dimeride $Te_2(C_{18}H_{36})_2$ has also been isolated in a crystalline condition and its molecular weight determined. This product, which resembles its selenium analogue, may contain two tellurium atoms in a 38-membered ring as shown in the above diagram. There was, however, no indication of a *cyclo*tellurohydrocarbon with a nineteen-membered ring.

Cyclic Selenohydrocarbons.

In collaboration with Mr. Burstall, a general method has been devised for the preparation of cyclic selenohydrocarbons, whereby an alkylene dihalide reacts with aqueous alcoholic sodium selenide in an inert atmosphere.

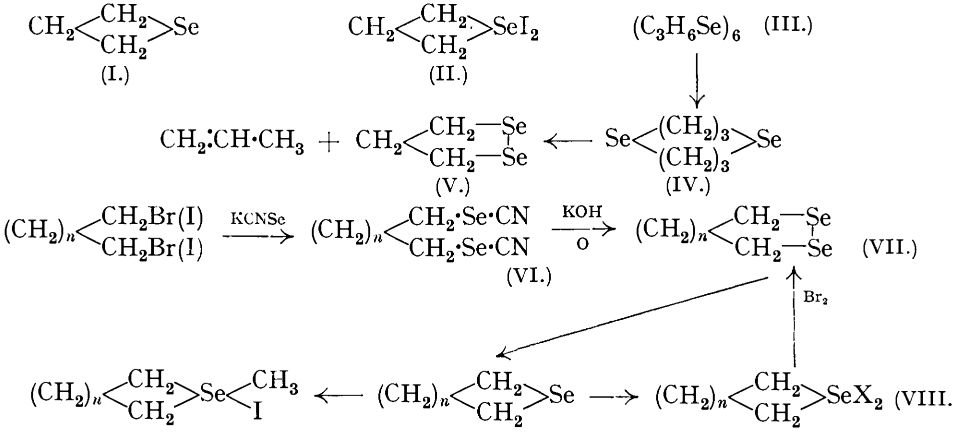
Cyclic Selenohydrocarbons. I.



$$(\mathrm{CH_2})_n{<}\begin{smallmatrix}\mathrm{CH_2Br}\\ \mathrm{CH_2Br}\end{smallmatrix} + \mathrm{Na_2Se} = (\mathrm{CH_2})_n{<}\begin{smallmatrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{smallmatrix}{>}\mathrm{Se} + 2\mathrm{NaBr}$$

$n = 1, 2, 3, 4,$ or 16

I. Small Rings.



$$\mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{smallmatrix}{>}\mathrm{Se}\ \text{(I.)} \qquad \mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{smallmatrix}{>}\mathrm{SeI_2}\ \text{(II.)} \qquad (\mathrm{C_3H_6Se})_6\ \text{(III.)}$$

$$\mathrm{CH_2{:}CH{\cdot}CH_3} + \mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{CH_2-Se}\\ \mathrm{CH_2-Se}\end{smallmatrix}\ \text{(V.)} \longleftarrow \mathrm{Se}{<}\begin{smallmatrix}(\mathrm{CH_2})_3\\ (\mathrm{CH_2})_3\end{smallmatrix}{>}\mathrm{Se}\ \text{(IV.)}$$

$$(\mathrm{CH_2})_n{<}\begin{smallmatrix}\mathrm{CH_2Br(I)}\\ \mathrm{CH_2Br(I)}\end{smallmatrix} \xrightarrow{\mathrm{KCNSe}} (\mathrm{CH_2})_n{<}\begin{smallmatrix}\mathrm{CH_2{\cdot}Se{\cdot}CN}\\ \mathrm{CH_2{\cdot}Se{\cdot}CN}\end{smallmatrix}\ \text{(VI.)} \xrightarrow[\mathrm{O}]{\mathrm{KOH}} (\mathrm{CH_2})_n{<}\begin{smallmatrix}\mathrm{CH_2-Se}\\ \mathrm{CH_2-Se}\end{smallmatrix}\ \text{(VII.)}$$

$$(\mathrm{CH_2})_n{<}\begin{smallmatrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{smallmatrix}{>}\mathrm{Se}{<}\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{I}\end{smallmatrix} \longleftarrow (\mathrm{CH_2})_n{<}\begin{smallmatrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{smallmatrix}{>}\mathrm{Se} \longrightarrow (\mathrm{CH_2})_n{<}\begin{smallmatrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{smallmatrix}{>}\mathrm{SeX_2}\ \text{(VIII.)}$$

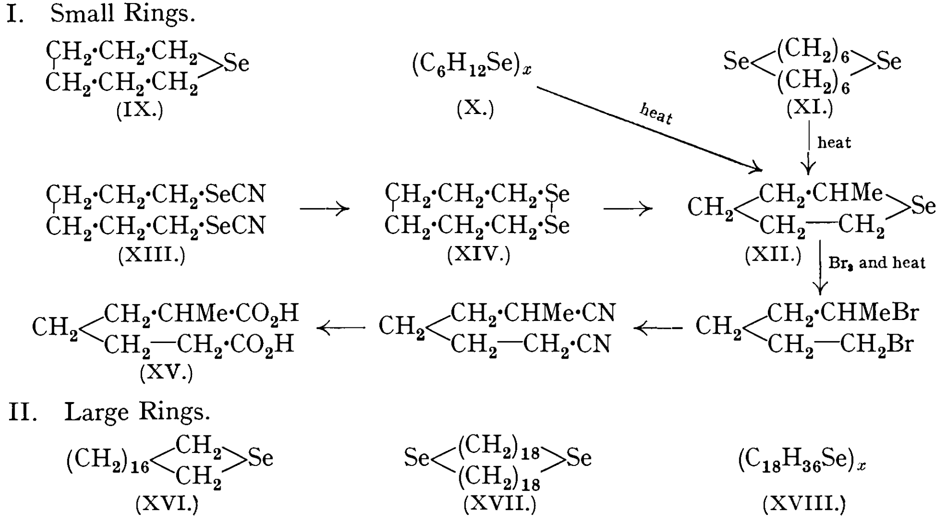
$n = 2$ or 3

X = Cl, Br, or I

Sodium selenide and 1 : 3-dibromopropane give only a low yield of *cyclo*selenopropane (I) as a readily decomposable liquid of pungent odour. Its di-iodide (II) is a deep purple substance of considerable stability. The main product of this condensation is, however, a six-fold polymeride (III), which on heating is depolymerised to the dimeride (IV). Further pyrolysis leads to *cyclo*-1 : 3-diselenopropane (V) with elimination of propylene.

cyclo*Selenobutane and* cyclo*Selenopentane.*—The two selenohydrocarbons containing five- and six-membered rings are both obtained in excellent yields by the general method. They are stable oils of pungent odour so similar in their chemical properties that the same diagram serves to illustrate their chemical deportment. This diagram indicates an alternative method of preparation based on the interaction of alkylene dihalides and potassium selenocyanate. The organic diselenocyanate (VI) is hydrolysed and oxidised simultaneously to a diselenide (VII), which on heating loses half its selenium and gives the *cyclo*-seleno-butane or -pentane. This partial removal of selenium may also be effected by the use of bromine, the dibromide (VIII) being obtained. The comparative instability of the seven-membered ring is indicated in the following diagram.

Cyclic Selenohydrocarbons. II.



The *cyclo*selenohexane (IX) is a minor product of the general reaction with sodium selenide. The main products are a polymeride of twelve-fold complexity (X), and a dimeride (XI) which probably contains two selenium atoms in a fourteen-membered ring. When these polymerides are heated, they undergo depolymerisation and rearrangement to give rise to 2-methyl*cyclo*selenopentane (XII), a six-membered ring compound which has also been obtained by the diselenocyanate method (XIII) through the eight-membered diselenide (XIV).

The constitution of 2-methyl*cyclo*selenopentane is demonstrated by a series of reactions leading to α-methylpimelic acid (XV), which was identified as its dianilide.

Although these results seem to indicate a limit of stability for the smaller rings at the seven-membered stage, further experiments have been made in order to ascertain whether selenium can be implicated in large rings. Condensation of 1 : 18-dibromo-octadecane and sodium selenide has led to the isolation of a small proportion of monomeric *cyclo*-seleno-octadecane (XVI), a nineteen-membered selenohydrocarbon, which is accompanied by a dimeride (XVII), probably containing two atoms of selenium in a 38-membered ring. The latter substance is analogous to a dimeric tellurium compound already described (p. 563). The main condensation product is, however, a polymeride of unknown complexity. The monomeric and dimeric compounds combine with iodine and mercuric chloride, but the addition products are unstable.

Aromatic Derivatives of Selenium and Tellurium.

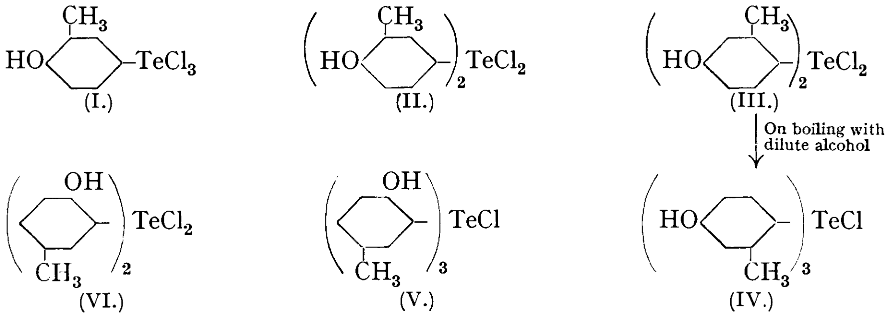
Selenium Oxychloride and Phenols.—A study with Mr. Burstall of the interactions of the phenols with selenium oxychloride has entailed a revision of earlier work by Michaelis and Kunckel, but a brief reference to the following diagram will indicate the present state of knowledge.

Selenium and Tellurium Derivatives containing Aryl Radicals.

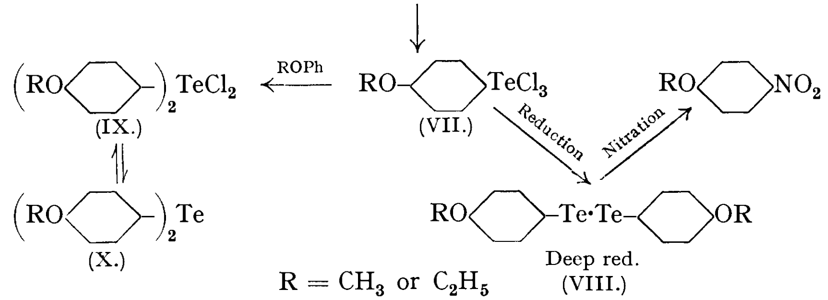
I. $3H{\cdot}R''{\cdot}OH + SeOCl_2 = (HO{\cdot}R'')_3SeCl + HCl + H_2O$
with phenol and resorcinol.

II. $3H{\cdot}R''{\cdot}OH + SeOCl_2 = Se(R''{\cdot}OH)_2 + Cl{\cdot}R''{\cdot}OH + HCl + H_2O$
with β-naphthol and salicylic acid.

o- and *p*-Cresols give both reactions.



Tellurium Tetrachloride and Anisole or Phenetole



$R = CH_3$ or C_2H_5

The foregoing workers examined the cases of phenol, β-naphthol and resorcinol and concluded that the two monohydric phenols gave diaryl selenides, $Se(R{\cdot}OH)_2$, whereas resorcinol was alleged to yield a selenyl derivative $SeO[C_6H_3(OH)_2]_2$. We were able to confirm these statements only in the case of β-naphthol, which furnishes di-2-hydroxydi-1-naphthyl selenide. Salicylic acid gives a similar disalicylyl selenide. Phenol actually gives rise to two trihydroxytriphenylselenonium chlorides, of which the main product is the tri-*p*-substituted compound, and resorcinol yields a similar selenonium chloride. With *o*- and *p*-cresols both types of interaction proceed concurrently, leading to trihydroxytritolylselenonium chlorides and to dihydroxyditolyl selenides.

Basic Tellurium Chloride and Phenols.—With basic tellurium chloride the cresols condense to give products still containing tellurium in combination with chlorine. *o*-Cresol gives a trichloride (I) and a dichloride (II). *p*-Cresol furnishes the polar trihydroxytritolyltelluronium chloride (V) and the non-polar dichloride (VI). *m*-Cresol yields a non-polar dichloride (III), which on boiling in alcoholic or feebly alkaline solution sheds one third of its tellurium and passes into the polar telluronium chloride (IV).

Tellurium Tetrachloride and Aromatic Ethers.—Tellurium tetrachloride reacts in a characteristic manner with the ethers of phenols and an examination of the products from anisole, phenetole and similar mixed ethers carried out with Dr. Drew and Mr. R. E. Kellett showed that earlier observations made by Rust and Rohrbaech in the Rostock Laboratories in 1897 and 1901 and those of Lederer made in Ghent during 1915 stand in need of considerable revision. Contrary to the earlier statements the initial product of the condensation with anisole or phenetole is a trichloride (VII) in which an aromatic radical has replaced only one of the chlorine atoms of tellurium tetrachloride. This trichloride when reduced with aqueous bisulphite furnishes the deep red bisaryl ditelluride (VIII). The true dichlorides (IX) were obtained by heating the trichlorides with excess of the corresponding aryl ether. These dichlorides on reduction gave rise to colourless diaryl tellurides (X). Here again one observes the development of colour consequent on the association of two bivalent tellurium atoms in the same molecule. These highly coloured aromatic ditellurides (VIII) may be regarded as analogues of azobenzene.

Extraction of Rare Metals from British Minerals.

Germanium and Gallium from Northumberland Coal Ash.

In 1933 it was observed by Goldschmidt and Peters that ash from many varieties of coal contains appreciable quantities of the rarer elements and in particular that certain seams in the Northumbrian coal fields gave an ash containing up to 1% of germanium. As this mineral residue appears to be a promising source of rare elements, its investigation has recently been started by Dr. G. R. Davies with the object of extracting from it germanium and any other rare elements which might be present.

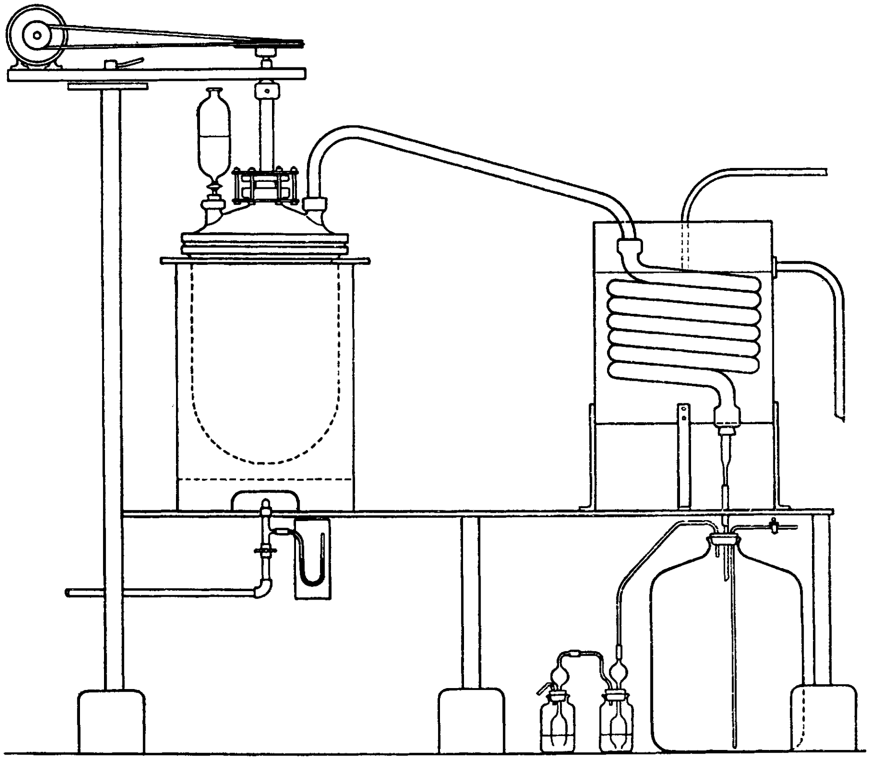
In this enquiry, which is still at a preliminary stage, it was found that the germanium content of the ash is extremely variable. The variation may be partly due to irregularities in the occurrence of the germaniferous mineral and partly to loss of germanium during incineration. Being more volatile than the dioxide, the lower oxide, GeO, might be volatilised away unless oxidising conditions prevail in the furnace.

As this Northumbrian ash may also contain up to about 0·05% of gallium, arrangements were made to extract both the rare elements. Germanium is probably present in the coal ash partly as sulphide and partly as oxide. Its extraction is accomplished by a distillation with concentrated hydrochloric acid, germanium tetrachloride passing over accompanied by arsenious chloride and sulphur.

The plant employed is shown in the figure. The still, which has a capacity of 20 litres, has a still-head fitted with stirrer and a delivery pipe leading to a water-cooled worm condenser. Owing to the corrosive nature of the acid, the still, still-head, stirrer, delivery pipe and condenser are all constructed of stoneware. The lower end of the condenser is connected in series with a demijohn of 25 litres capacity, and two wash-bottles, the latter containing aqueous *N*-caustic soda.

About 14 lb. of finely divided ash are introduced into the still with 6 litres of concentrated hydrochloric acid (*d* 1·16) and an equal volume of 20% acid. This acid mixture is so adjusted that after neutralising the metallic oxides its strength is slightly less than that of the constant-boiling mixture. The still is heated in a gas-fired oil-bath, and the distillation continued for about 30 hours or until a test sample of 150 c.c. gives no precipitate after saturation with hydrogen sulphide. From time to time 20% hydrochloric acid is added in order to replace the loss by distillation. About 10—12 litres of distillate are collected, leaving a residue of 5—6 litres of liquid mixed with a sludge of mineral residue and unburnt coal. The distillate is conveyed to two 10-litre flasks, the liquid from the two wash-bottles added, and the germanium precipitated as white sulphide. After 12 hours' settling, the supernatant liquid is air blown to remove hydrogen sulphide and utilised in subsequent distillations. The moist precipitate of germanium sulphide, which is contaminated with sulphur and arsenious sulphide, is dissolved in 5*N*-sodium hydroxide, and the solution redistilled with hydrochloric acid in a stream of chlorine. Arsenic is thus restored to the quinquevalent condition and rendered much less volatile. The oily germanium tetrachloride in the distillate is either hydrolysed to hydroxide or subjected again to the preceding operations and the purified sulphide hydrolysed to hydrated oxide by boiling with water in a current of carbon dioxide.

Any gallium present in the ash remains in the still as trichloride and is separated from the large excess of iron by ether extraction according to Swift's method (*J. Amer. Chem. Soc.*, 1924). For this separation the iron must be present in the ferrous condition, which is mainly the case, but reduction is completed by zinc or hydrogen sulphide. The still liquor is then extracted with ether for 4 days, a layer of mercury being placed at the base of the extractor to prevent aerial oxidation. In spite of this precaution some ferrous salt is oxidised to ferric chloride, which dissolves in the ether. After removal of ether from the extract the dissolved chlorides are converted into sulphates and these salts are dissolved in a large bulk of water. This solution, almost neutralised with sodium carbonate, is boiled with sodium thiosulphate, neutralisation being completed with aniline (Moser and Brukl, 1929). The crude gallium oxide is redissolved in dilute sulphuric acid and the iron present is reduced to the ferrous state. The solution is neutralised partly with sodium carbonate and completely by boiling with cuprous oxide. The precipitate of crude oxide is again dissolved in dilute sulphuric acid, and excess of copper removed with hydrogen sulphide. Addition of ammonia to the concentrated filtrate precipitates gallium hydroxide, which is ignited to gallia.

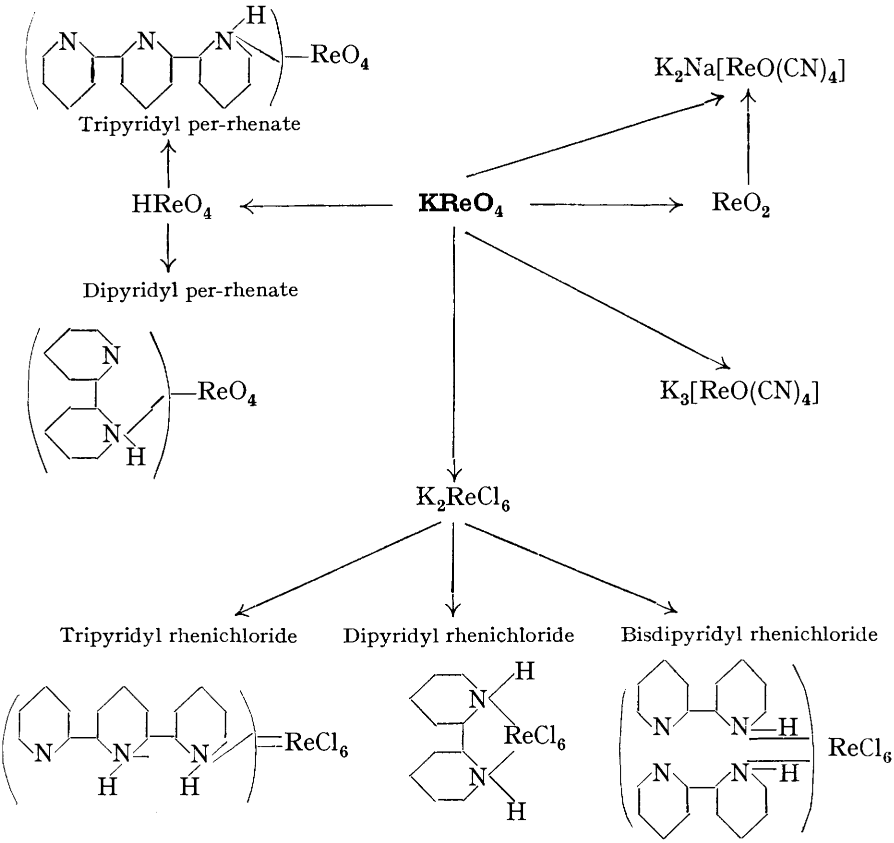


Rhenium from Australian Molybdenite.

As Australian molybdenite has not previously been tested for rhenium, a detailed examination of this mineral has been made to ascertain whether it could be used as a convenient source of the rare element. This molybdenite in batches of 11—13 lb. was treated with 20—22 litres of nitric acid (*d* 1·4) in a steam-jacketed tantiron pan until 50 lb. of mineral had been used. Oxidation proceeded rapidly with copious evolution of nitrous fumes and sulphur dioxide. The temperature, which rose to 75° or 80°, was maintained by external heat. The resulting greyish-white mass was made up to 90 litres with water, and molybdenum trioxide collected with a porcelain stream-line filter and washed in a filter press. The total filtrate, now amounting to about 85 litres, was concentrated in a steam-jacketed enamelled pan. As evaporation proceeded, more trioxide separated and at 22 litres the solution was diluted with its own bulk of water, neutralised with aqueous ammonia (*d* 0·88), and treated with sodium phosphate and sufficient nitric acid to precipitate yellow ammonium phosphomolybdate, which was collected after 2 days. The filtrate, neutralised with ammonia, was treated successively with ammonium sulphide and dilute sulphuric acid to precipitate mixed sulphides of molybdenum and rhenium, which were dissolved in nitric acid and the solution evaporated with sulphuric acid. This concentrated solution was distilled in hydrogen chloride up to 200° ; the distillate when passed into water gave a solution of the hydrated oxides of molybdenum and rhenium. In this distillation molybdenum volatilised much more slowly than rhenium and a repetition of the process led to a considerable separation, which was completed by means of 8-hydroxyquinoline and nitron. The former reagent precipitated molybdenum, the latter produced sparingly soluble nitron per-rhenate.

Complex Salts of Rhenium.

Until quite recently, complex double cyanides of rhenium were unknown but in 1932 a paper appeared by a Polish chemist Turkiewicz describing a compound of this series as $K_3[ReO(CN)_4 \cdot OH]$, prepared by the action of aqueous potassium cyanide on rhenium dioxide. In our experiments potassium per-rhenate, potassium cyanide and hydrazine hydrate were heated together in aqueous solution, from which alcohol subsequently deposited pale pinkish-yellow crystals of $K_2Na[ReO(CN)_4]$. The presence of sodium was due to the use of commercial cyanide, and further experiments with purified potassium salts gave the tripotassium cyanide $K_3[ReO(CN)_4]$.



The dipyridyl salts shown in the diagram may serve to separate rhenichloric acid from per-rhenic acid. 2 : 2′-Dipyridyl rhenichloride, which crystallises in yellow needles, arises from the interaction of its generators in hydrochloric acid. Bis-2 : 2′-dipyridyl rhenichloride is obtained in pale green, acicular crystals when potassium rhenichloride and 2 : 2′-dipyridyl react in dilute acetic acid. Both salts are sparingly soluble in cold water. 2 : 2′-Dipyridyl per-rhenate is formed on addition of 2 : 2′-dipyridyl in dilute acetic acid to a concentrated aqueous solution of per-rhenic acid. It crystallises in leaf-like clusters of colourless lustrous needles and is more soluble in cold water than the preceding rhenichloride, since 2·1 grams will dissolve in 100 c.c. of water. 2 : 2′ : 2″-Tripyridyl also gives characteristic salts with the two rhenic acids. With rhenichloric acid it yields only one salt, 2 : 2′ : 2″-tripyridyl rhenichloride, whether the combination is effected in acidic or almost neutral solutions. The colourless product, which dries to a pale green, microcrystalline powder, is practically insoluble in cold water.

2 : 2′ : 2″-Tripyridyl per-rhenate was prepared from its generators in warm dilute acetic acid as a white crystalline precipitate considerably less soluble in cold water than either the dipyridyl salt or potassium per-rhenate.

During the examination of Australian molybdenite, 2 : 2′-dipyridyl was employed in the final separation of molybdenum and rhenium from a mixture containing 10 parts of Mo to one part of Re. It precipitated 99·5% of the former metal as dipyridyl molybdate, and left in solution 99·6% of the rhenium originally present.

Co-ordinated Ruthenium Compounds.

Early researches on the ammines of ruthenium were made by Claus, the discoverer of this metal (1846), and later these complex salts were studied by Joly (1892 *et seq.*). The latter investigator found that ruthenium trichloride prepared by direct synthesis at 380—400° absorbed ammonia to form $Ru_2Cl_6,7NH_3$, a substance dissolving in water to an intensely red solution. The colouring matter of this liquid, which is known as "ruthenium red," dyes natural silk in red shades. This highly coloured substance is extremely difficult to obtain in a state of purity. The formula $Ru_2(OH)_2Cl_4,7NH_3,3H_2O$ ascribed to it by Joly is scarcely in conformity with modern views on co-ordination.

Ethylenediamine dissolves ruthenium trichloride to form a red solution, but in this case also it is difficult to obtain definite crystalline derivatives. There is no evidence of a similar combination of ruthenium trichloride with 2 : 2′-dipyridyl.

A more promising starting point for the preparation of well-defined co-ordinated ruthenium salts is potassium nitrosoruthenochloride, $K_2[RuNOCl_5]$, an analogue of the well-known potassium nitroprusside, $K_2[FeNO(CN)_5]$. When this ruthenium salt reacts with 2 : 2′-dipyridyl, two non-ionised compounds are obtained having the structural formula (I). These two isomerides, which are green and reddish-brown respectively, may be obtained at will by suitably adjusted experimental conditions.

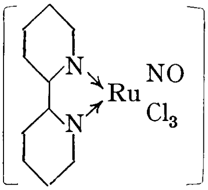
By analogy with the corresponding ethylenediamine compounds (Charonnat, 1931) it is suggested that the red form has the *trans*-configuration (II) and the green form the *cis*-arrangement. Both modifications dissolve in aqueous solutions of such bases as ammonia, ethylenediamine, pyridine, and 2 : 2′-dipyridyl, but the resulting tetrammines are extremely soluble and difficult to isolate.

By employing potassium nitrosoruthenobromide and the corresponding iodide the complex brown tribromide (IV) and black tri-iodide (V) were each obtained but only in one modification. In acid solutions, potassium nitrosoruthenochloride and 2 : 2′-dipyridyl give rise to deep purple crystals of the dipyridyl salt (VI).

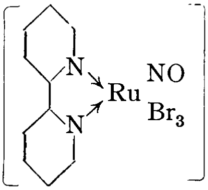
A dipyridyl compound of the hydroxo-series is obtained as follows : A solution of 2 : 2′-dipyridyl in dilute hydrochloric acid is added to a solution of the ruthenium chlorides prepared by dissolving hydrated ruthenium oxide in concentrated hydrochloric acid, and chlorine is introduced in order to bring ruthenium to the quadrivalent condition. At this stage the dipyridyl hydroxyruthenichloride (VII) separates in dark brown crystals.

When the tridentate base, 2 : 2′ : 2″-tripyridyl, reacts with potassium nitrosoruthenochloride, two products are obtained, first a soluble chloride (VIII) crystallising with one or four molecules of water, and secondly an insoluble complex salt (IX) containing the nitrosoruthenochloride anion.

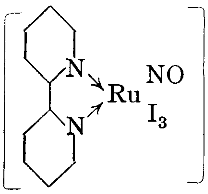
2 : 2′-Dipyridyl Ruthenium Compounds.



Green and red forms.
(I.)

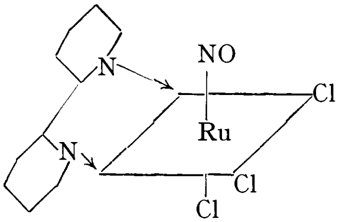


Brown.
(IV.)

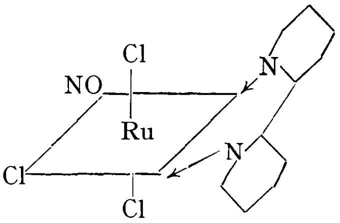


Black.
(V.)

(II.)

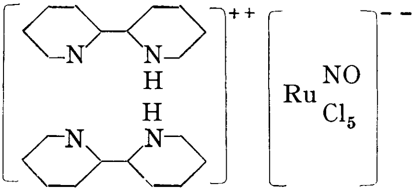


Red (*trans*).

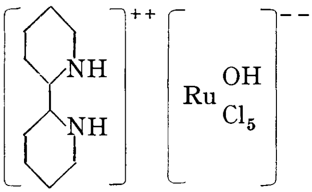


(III.)

Green (*cis*).

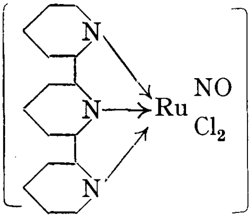


(VI.)



(VII.)

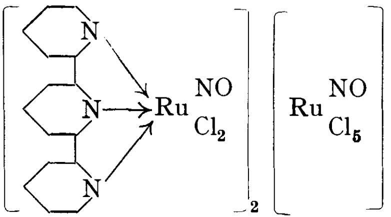
2 : 2′ : 2″-Tripyridyl Ruthenium Compounds.



Cl,xH$_2$O

$x = 1$ or 4

(VIII.)



(IX.)

In pursuing these investigations on ruthenium derivatives we have been greatly assisted by a loan of the metal from the Mond Nickel Company, to whom we desire to express our cordial thanks. The rutheniferous mineral is of British origin, for it was obtained from the Company's mines in Sudbury, Ontario, Canada.

In this Year of Jubilee and national rejoicing I would like to refer to the fact that the British Empire is endowed with mineral resources to an extent unsurpassed by those of any other nation or empire under the sun. These valuable assets involve us in a great responsibility and we ought not to leave the work of exploration entirely to others. A systematic study of the rare elements of the Empire should be a first call on the activities of British chemists. Such researches cannot fail to be of scientific interest and, as in the past, discoveries will from time to time be made in the application of these materials which will redound to the credit of our science and to the good of the community.