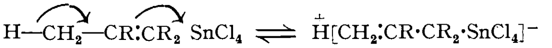
189. *α-Methylenic Reactivity in Olefinic Systems. Part II. The Reaction between Olefins and Phenyl* iso*Cyanate: Evidence relating to the Catalytic Action of Stannic Chloride.*

By John W. Baker and J. B. Holdsworth.

In the presence of anhydrous stannic chloride, olefins of the general type $CH_3{\cdot}CR{:}CR_2$ (R = H or alkyl) readily undergo polymerisation to give polymers $(CH_2)_n$ of varying degrees of molecular complexity, but when phenyl *iso*cyanate is also present this main polymerisation reaction is accompanied by another, probably much slower, reaction which results finally in the formation of *NN′N″*-triphenylbiuret (I) in very small yield. Under the rigorously anhydrous conditions employed, the hydrogen necessary for the formation of (I) must be derived from the olefin, and this is confirmed by the observation that no reaction occurs when the olefin is replaced by the corresponding saturated paraffin. The initial step in the formation of (I) is most probably the direct addition of the olefin, behaving as a hydrogen acid $\overset{+}{H}[CH_2{:}CR{\cdot}CR_2]^-$, to phenyl *iso*cyanate to form the unsaturated acid anilide $CR_2{:}CR{\cdot}CH_2{\cdot}CO{\cdot}NHPh$. A reaction mechanism involving the subsequent "olefinolysis" of this anilide to give aniline and thence carbanilide and (I) is suggested, and experimental verification of each of the postulated steps is detailed. During the course of the investigation solid comple compounds of anhydrous stannic chloride with (1) aniline, (2) carbanilide and (3) vinylacetanilide have been isolated and analysed, and their further reactions with dry phenyl *iso*cyanate have been studied. Preliminary investigations of the structure of the dimeride of trimethylethylene are described.

In continuation of the investigations initiated in Part I (Baker, J., 1944, 296) to ascertain the extent to which hydrogen, activated solely by the hyperconjugation in an olefin $H\text{—}\overset{\curvearrowright}{CH_2\text{—}}CR\overset{\curvearrowright}{=}CR_2$, can undergo the reactions of "classically" activated hydrogen (*e.g.* in the system $H\text{—}\overset{\curvearrowright}{CH_2\text{—}}C\overset{\curvearrowright}{=}O$), the reaction between olefins and phenyl *iso*cyanate has now been studied. No appreciable reaction occurs between these two reagents in the absence of catalysts. Peroxidic catalysts are ineffective and alkaline catalysts, which might directly assist the removal of the α-methylenic hydrogen, are excluded, since they cause rapid polymerisation of the *iso*cyanate to the crystalline trimeride, $(PhNCO)_3$. Attention was accordingly directed towards non-hydrogen acids of the Lewis type (*J. Franklin Institute*, **1938**, **226**, 293) such as anhydrous stannic chloride, which is known to be a powerful acceptor of electron-pairs. When a pure, sodium-dried olefin, such as trimethylethylene, is added to anhydrous stannic chloride, the mixture of the colourless liquids assumes a pale greenish colour, indicative that some reaction occurs. It is suggested that this reaction is possibly of a type tending towards the conversion of the olefin into a strong hydrogen acid thus :



$$H—CH_2—CR{:}CR_2\ SnCl_4 \rightleftharpoons \overset{+}{H}[CH_2{:}CR{\cdot}CR_2{\cdot}SnCl_4]^- \quad (II.)$$

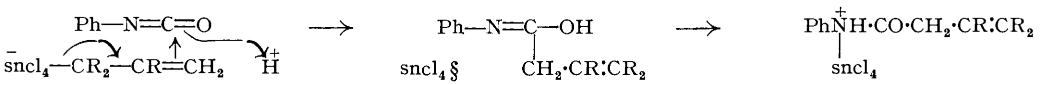
(cf. Meerwein, *Annalen*, 1927, **455**, 227). Little actual ionisation may result in the olefin–stannic chloride compound and the equilibrium is probably displaced largely to the left. In fact, no current is detectable on a sensitive microammeter when a potential of 100 volts (D.C.) is applied through an approximately 4 c.c. column of a dry trimethylethylene–stannic chloride solution, the resistance of which is thus $> 10^7$ ohms. The essential change is the acceptance of an electron-pair by the stannic chloride, thus resulting in a further weakening of the H–C bond of the α-methylenic group and a considerable increase in the ionising power of the proton, a change which should greatly facilitate any subsequent reaction which is dependent upon proton addition; addition to phenyl *iso*cyanate is of this type.

When an olefin of the general type $H—CH_2{\cdot}CR{:}CR_2$ is allowed to react with phenyl *iso*cyanate in the presence of anhydrous stannic chloride for periods up to seven days at room temperature under experimental conditions which rigidly exclude all traces of water (see p. 728) small yields * of *NN′N″*-triphenylbiuret (I) can be isolated from the non-volatile, tin-containing products of the reaction. This product (I) has thus been isolated or identified in the products of such reactions with the following olefins : propylene, trimethylethylene, tetramethylethylene, αα-diphenyl-Δ^{α}-propene, *cyclo*hexene and 2-methyl-Δ^1-*cyclo*hexene. The formation of (I) was rather unexpected since it was anticipated that, if reaction occurred at all, the product would be the anilide of the unsaturated acid, $CR_2{:}CR{\cdot}CH_2{\cdot}CO{\cdot}NHPh$. Hence preliminary experiments were undertaken which proved that (1) carbanilide and phenyl *iso*cyanate do not combine together at room temperature † in the absence of a catalyst, but addition of anhydrous stannic chloride to a suspension of dry carbanilide in dry phenyl *iso*cyanate causes dissolution of the carbanilide (with slight evolution of heat), and the reaction mixture, kept sealed for several days, deposits *NN′N″*-triphenylbiuret in good yield : (2) phenyl *iso*cyanate and anhydrous stannic chloride do not react when they are sealed together for seven days, but the materials distil together, apparently unchanged, leaving no residue.

The formation of the biuret in the olefin reaction must therefore involve some subsequent fission of the initial product, the unsaturated acid anilide, to give aniline, the reaction of this aniline with phenyl *iso*cyanate to yield carbanilide and the further reaction of the carbanilide with more *iso*cyanate (catalysed by stannic chloride) to give the final product, *NN′N″*-triphenylbiuret. The most interesting stage in this sequence is the fission of the unsaturated anilide, for which the only possible reagent is the olefin–stannic chloride acid (II). Such " olefinolysis " of several unsaturated acid anilides, to give good yields of free aniline, has been experimentally demonstrated.

Verification of the initial hypothesis of the formation of the acid-type $\overset{+}{H}[CH_2{:}CR{\cdot}CR_2{\cdot}SnCl_4]^-$ is difficult; any evidence must almost certainly be based on physical properties (dipole moment, spectra, etc.) and this aspect is under investigation.‡ If this initial step is assumed, it provides an adequate basis for a sequence of reactions which together prescribe a mechanism leading to the ultimate formation of *NN′N″*-triphenylbiuret in the olefin-*iso*cyanate-stannic chloride reaction. The suggested scheme is given below where, for simplification, the ionised, olefin-stannic chloride complex (II) is employed. Each postulated stage has been demonstrated experimentally.

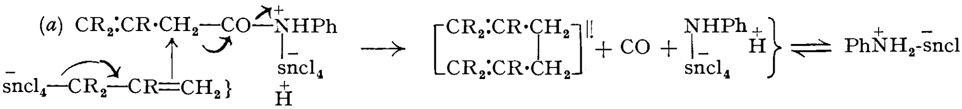
I. *Interaction of olefin-stannic chloride acid with phenyl* iso*cyanate to yield the unsaturated anilide.*



$$\begin{matrix} Ph—N{=}C{=}O \\ \bar{s}ncl_4—CR_2—CR{=}CH_2 \quad \overset{+}{H} \end{matrix} \longrightarrow \begin{matrix} Ph—N{=}C—OH \\ sncl_4\,\S \quad\ \ CH_2{\cdot}CR{:}CR_2 \end{matrix} \longrightarrow \begin{matrix} Ph\overset{+}{N}H{\cdot}CO{\cdot}CH_2{\cdot}CR{:}CR_2 \\ | \\ sncl_4 \end{matrix}$$

II. " *Olefinolysis* " *of the anilide with the olefin–stannic chloride acid.* Two alternative schemes are possible (cf. also p. 727) :

Either



$$(a)\ \begin{matrix} CR_2{:}CR{\cdot}CH_2—CO—\overset{+}{N}HPh \\ \qquad\qquad\qquad\qquad\quad |_- \\ \qquad\qquad\qquad\qquad\quad sncl_4 \\ \bar{s}ncl_4—CR_2—CR{=}CH_2\} \quad \overset{+}{H} \end{matrix} \longrightarrow \begin{bmatrix} CR_2{:}CR{\cdot}CH_2 \\ | \\ CR_2{:}CR{\cdot}CH_2 \end{bmatrix}^{\|} + CO + \left.\begin{matrix} NHPh \\ |_- \qquad \overset{+}{H} \\ sncl_4 \end{matrix}\right\} \rightleftharpoons Ph\overset{+}{N}H_2\text{-}\bar{s}ncl_4$$

---

* The small yields are probably prescribed by the much more rapid polymerisation reaction of the olefin. On theoretical grounds it is apparent that the same structural factors which might be expected to increase the reactivity of an olefin towards phenyl *iso*cyanate would also facilitate the polymerisation reaction.

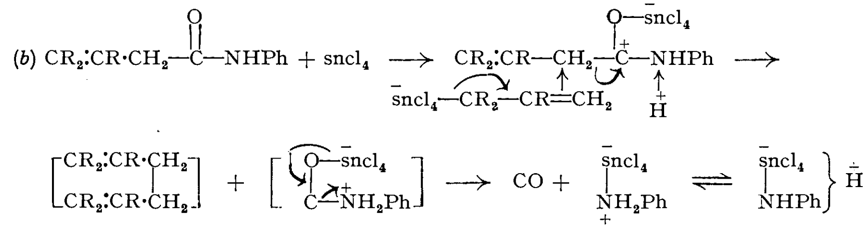
† Addition to give the biuret is stated to occur when the reactants are heated together (Kühn and Henschell, *Ber.*, 1888, **21**, 504).

‡ Dr. F. Fairbrother (University of Manchester) has since informed one of us (J. W. B.) that he is investigating the dielectric polarisation of olefin–stannic halide mixtures. His results should provide the necessary information.

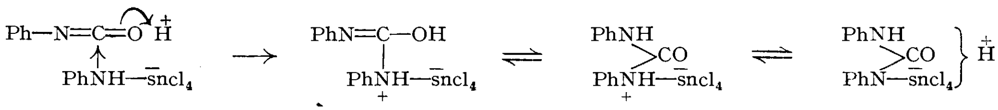
§ The molecular proportions in the various (isolated) stannic chloride complexes have been shown by actual analysis to vary from compound to compound : the general expression " $sncl_4$ " has been used to represent that proportion of the $SnCl_4$ molecule which is stoicheiometrically associated with *one* molecule of the other component.

‖ Such an unsaturated diolefin would almost certainly undergo further polymerisation in the presence of stannic chloride. Its presence would, therefore, be difficult to detect owing to the presence, in the reaction products, of the mixture of polymerides resulting from the direct polymerisation of the original olefin.

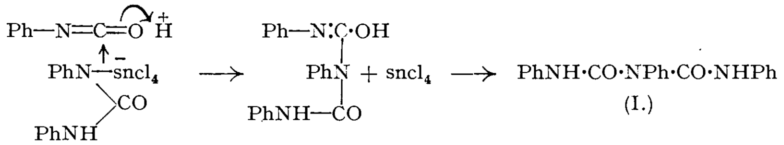
or



III. *Condensation of aniline–stannic chloride complex with* PhNCO *to give the carbanilide complex.*



IV. *Condensation of carbanilide–stannic chloride complex with* PhNCO *to give* NN'N''*-triphenylbiuret.*



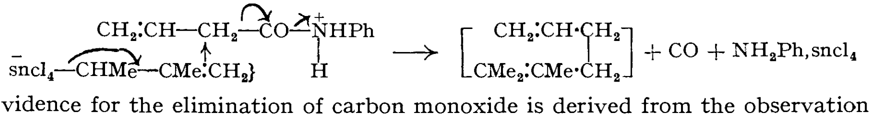
It has been shown that (I) does not form an additive complex with stannic chloride, hence this final product crystallises out or remains in solution.

The experimental evidence in support of each step in the postulated mechanism is summarised below.

I. *Formation of the unsaturated acid anilide.* Owing to its subsequent reaction with the olefin–stannic chloride acid, it has not been found possible to isolate this assumed initial product, but the evidence given under (II) proves that such unsaturated anilides do react farther, in accordance with the suggested scheme (cf. also p. 729).

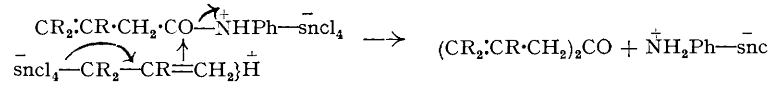
II. " *Olefinolysis* " *of the unsaturated anilide.* The simplest unsaturated acid anilide, vinylacetanilide (the expected initial product from the interaction of propylene with phenyl *iso*cyanate) was kept sealed with anhydrous stannic chloride and trimethylethylene for four days at room temperature. The gaseous products of the reaction showed the presence of carbon monoxide by the reduction of a freshly prepared solution of silver oxide in pyridine (Manchot and Scherer, *Ber.*, 1927, **60**, 326). After removal of volatile materials the residual tin-containing solid, decomposed by cold aqueous sodium carbonate, yielded free aniline (characterised as benzanilide) corresponding to appreciable fission of the original anilide used. Control experiments proved that no hydrolysis of the vinylacetanilide occurs under any of the conditions used in the isolation of the aniline from the reaction tin-complex. A similar olefinolysis of the anilide of pyroterebic acid, $CMe_2{:}CH{\cdot}CH_2{\cdot}CO{\cdot}NHPh$ (one of the two possible initial products from the interaction of trimethylethylene with phenyl *iso*cyanate; Goldberg and Linstead, *J.*, 1928, 2354), gave free aniline corresponding to approximately 70% fission of the anilide. The *anilide*, $CHMe{:}CMe{\cdot}CH_2{\cdot}CONHPh$, of β-methyl-$\Delta^{\beta}$-pentenoic acid (the alternative possibility) was more resistant to fission, only 10% olefinolysis occurring in six days. Under the same anhydrous conditions no reaction occurred in four days between vinylacetanilide and trimethylethylene alone, whereas vinylacetanilide and stannic chloride alone give no aniline but form an unstable solid *complex*, $CH_2{:}CH{\cdot}CH_2{\cdot}CO{\cdot}NHPh{\cdot}SnCl_4$, which is decomposed by aqueous sodium carbonate to regenerate the original anilide. Vinylacetanilide reacts with dry phenyl *iso*cyanate at room temperature giving *vinylacetylcarbanilide* and, depending on the relative speeds of the various reactions, this compound may alternatively be the entity which undergoes olefinolysis in the ultimate formation of triphenylbiuret.

Decomposition with sodium carbonate of the volatile materials from the olefinolysis of vinylacetanilide gave a small amount of a hydrocarbon which, on ozonolysis, afforded formaldehyde. The polymeric products from the trimethylethylene alone give only acetaldehyde (CHMe: end group) on ozonolysis and no formaldehyde (see p. 731). The presence of the latter compound in the hydrocarbon product from the olefinolysis of vinylacetanilide confirms the presence of a $CH_2{:}$ end group, thus indicating that the allyl chain of the anilide is transferred to the hydrocarbon reaction product in agreement with the suggested mechanism :



Further evidence for the elimination of carbon monoxide is derived from the observation that monomeric *cyclo*pentadiene reacts so vigorously and rapidly with phenyl *iso*cyanate in the presence of anhydrous stannic chloride (to give a dark mass, mainly an amorphous rubbery polymeride and some carbanilide), that the gaseous products can readily be collected in a Hempel burette and can be proved to consist largely of carbon monoxide both by the pyridine–silver oxide reduction and by actual combustion with the characteristic blue flame.

There is just the possibility that fission in the olefinolysis of the unsaturated acid anilide might occur only between the CO–¦–NHPh groups, in which case the initial products would be aniline and an unsaturated ketone,



$$\begin{array}{l}\mathrm{CR_2{:}CR{\cdot}CH_2{\cdot}CO{-}\overset{+}{N}HPh{-}\overset{-}{s}ncl_4}\\ \mathrm{\overset{-}{s}ncl_4{-}CR_2{-}CR{=}CH_2\}\overset{+}{H}}\end{array} \longrightarrow \mathrm{(CR_2{:}CR{\cdot}CH_2)_2CO + \overset{+}{N}H_2Ph{-}\overset{-}{s}ncl_4.}$$

Although frequently sought with 2 : 4-dinitrophenylhydrazine, no trace of carbonyl reactivity could be detected in any of the reaction products. Moreover, it was demonstrated that the simple unsaturated ketone, ethyl allyl ketone (Blaise, *Bull. Soc. chim.*, **1905**, **33**, 40) is decomposed, under anhydrous conditions, by trimethylethylene-stannic chloride, and that all the products are completely devoid of ketonic activity. Inconclusive evidence for the presence of carbon monoxide in the gaseous products was obtained.

The aniline liberated in the olefinolysis is combined as a complex with stannic chloride and this complex was actually isolated from the reaction products. Moreover it was shown that pure dry aniline reacts instantly with anhydrous stannic chloride to form a stable solid white *complex*, $2C_6H_5NH_2,SnCl_4$.

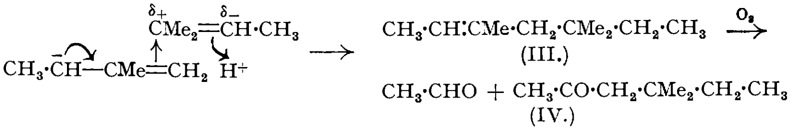
III. *Condensation of the aniline-stannic chloride complex with phenyl* iso*cyanate to give carbanilide-stannic chloride complex and* NN′N″*-triphenylbiuret.* When the dry aniline-stannic chloride complex is kept sealed with pure dry phenyl *iso*cyanate for four days the resulting white solid product affords *NN′N″*-triphenylbiuret when repeatedly extracted with boiling ligroin (b. p. 40—60°); and the ligroin-insoluble tin-containing residue affords carbanilide when decomposed by crystallisation from boiling methyl alcohol. Thus, both carbanilide and *NN′N″*-triphenylbiuret are formed in good yield in the reaction.*

When pure dry carbanilide is left sealed with anhydrous stannic chloride for a few hours at room temperature, removal of the excess of stannic chloride leaves a moderately stable, solid *complex*, $3[CO(NHPh)_2],2SnCl_4$.

IV. *Condensation of the carbanilide–stannic chloride complex with phenyl* iso*cyanate to give* NN′N″*-triphenylbiuret.* The solid carbanilide-stannic chloride complex similarly reacts with dry phenyl *iso*cyanate at room temperature to give *NN′N″*-triphenylbiuret, isolated in good yield after removal of the excess phenyl *iso*cyanate and liberated stannic chloride. The triphenylbiuret seems not to form a complex since it was recovered unchanged after it had been kept sealed with anhydrous stannic chloride for several weeks.

The experimental verification of each step in the reaction scheme suggested on p. 725 is thus complete, but it is essential to prove that the initial formation of carbanilide could not arise from traces of moisture present in the reaction vessel. The vigorous technique employed (see p. 728) renders such an explanation of the results highly improbable. It is completely excluded by the observation that when the trimethylethylene–phenyl *iso*cyanate–stannic chloride reaction was repeated in the same apparatus and using exactly the same technique but with dry *iso*pentane in place of the olefin no trace of either carbanilide or triphenylbiuret was obtained. The whole reaction mixture distilled leaving no solid residue and the condensed volatile distillate accounted for 97% of the total materials used. The presence of the olefin is thus essential for the formation of the triphenylbiuret. The main function of the stannic chloride catalyst would appear to be greatly to increase the importance of no-bond structures of the type $\overset{+}{\mathrm{H}}\ \mathrm{CH_2{=}CR{-}\overset{-}{C}R_2}$ in the resonance hybrid (cf. Part I, *loc. cit.*) by virtue of its strong affinity for electron pairs.

Only a very preliminary investigation of the polymeric olefin products has so far been made. In the case of trimethylethylene three distinct fractions have been isolated, all in small amounts : (i) b. p. *ca.* 55°/15 mm., (ii) b. p. *ca.* 110°/14 mm. and (iii) b. p. *ca.* 105°/0·6 mm. All three fractions are represented by the general formula C_nH_{2n} and are thus self-addition products of the olefin. Ozonolysis of the fraction of lowest boiling point affords acetaldehyde and a ketone with a camphoraceous odour which gives a *semicarbazone* $C_9H_{19}ON_3$, m. p. 159°. The ketone is thus $C_8H_{16}O$. If, as is likely, this is a methyl ketone, it would be a methyl hexyl ketone and the structure of the dimeric hydrocarbon would be $C_6H_{13}{\cdot}CMe{:}CHMe$. No reliable information regarding the structure of the C_6H_{13} group is yet available, but it is of interest to note that a structure (III) which satisfies the above data, would result from the addition of the " no-bond " structure of one molecule of the olefin to a second molecule the double bond of which is polarized in the normal direction :



$$\begin{array}{l}\mathrm{\overset{\delta+}{C}Me_2{=}\overset{\delta-}{C}H{\cdot}CH_3}\\ \mathrm{CH_3{\cdot}\overset{-}{C}H{-}CMe{=}CH_2\ \ H^+}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH_3{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_3} \xrightarrow{O_3}\\ \text{(III.)}\\ \mathrm{CH_3{\cdot}CHO + CH_3{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_3}\\ \text{(IV.)}\end{array}$$

The ketone, δδ-dimethyl-*n*-hexan-β-one (IV), has been synthesised (by ketonic hydrolysis of *ethyl* tert.-*amylacetoacetate*). It has a camphoraceous odour and forms a *semicarbazone*, m. p. 173°, which, however, raises the m. p. of the semicarbazone, m. p. 159°, from the ozonolysis product. Quantities of material at present available are insufficient to determine whether the two semicarbazones are different or are stereoisomerides derived from identical ketones, and a fuller investigation of the structure of the polymerides of trimethylethylene is in hand.

---

* Interaction of the stannic chloride complexes of different bases with various *iso*cyanates opens up an interesting field of investigation on the formation of unsymmetrically tri-substituted biurets and on their thermal decomposition products, and it is intended to explore this field in future work.

EXPERIMENTAL.

Preparation of materials. Propylene was prepared by dehydration of *n*-propyl alcohol with concentrated sulphuric acid and anhydrous aluminium sulphate at 110° (Senderens, *Bull. Soc. chim.*, 1911, [iv], **9**, 373). The gas was dried, condensed with solid carbon dioxide-acetone and collected in a Dewar vessel from which it was slowly distilled and collected as a gas in a water-filled gasometer. The gas was dried by passage through a phosphorus pentoxide drying train before entering the reaction medium.

Trimethylethylene was prepared by dehydration of synthetic dimethylethylcarbinol (from acetone and magnesium ethyl bromide) with anhydrous oxalic acid, and was purified by repeated fractionation over clean sodium, b. p. 37—37·5°/760 mm.

Tetramethylethylene, b. p. 70—72°/766 mm., was similarly prepared from synthetic dimethyl*iso*propylcarbinol (Ingold, *J.*, 1937, 1039).

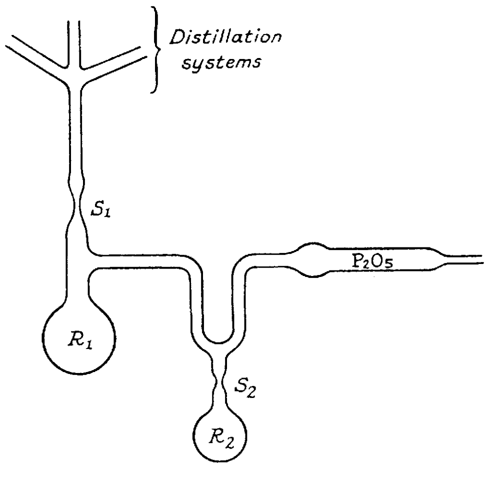
αα-Diphenyl-Δ^{α}-propene, m. p. 52°, was obtained by dehydration of synthetic diphenylethylcarbinol with potassium hydrogen sulphate at 170°. A purchased specimen of *cyclo*hexene was fractionated over sodium and a sample, b. p. 83°/763 mm. was used. 2-Methyl-Δ^{1}-*cyclo*hexene, b. p. 108°, was prepared by dehydration of synthetic 1-methyl*cyclo*hexanol (from *cyclo*hexanone and magnesium methyl iodide) with potassium hydrogen sulphate.

Vinylacetic acid (Linstead, Noble and Boorman, *J.*, 1933, 560) was converted into its acid chloride and thence into its anilide by Autenreith's method (*Ber.*, 1905, **38**, 2547). Crystallised from ligroin,* it had m. p. 61° (*lit.* m. p. 58°).

Pyroterebic acid and its anilide were prepared by the synthetic method of Goldberg and Linstead (*J.*, 1928, 2354).

Ethyl β-hydroxy-β-methylvalerate was prepared by a Reformatsky reaction using 36 g. of methyl ethyl ketone, 83 g. of ethyl bromoacetate and 32·5 g. of zinc wool in 100 c.c. of sodium dried benzene. The hydroxy-ester (34 g.) b. p. 83—85°/16 mm., was heated with powdered, anhydrous potassium hydrogen sulphate (45 g.) at 170—180° for 2 hours. Isolation in the usual manner gave ethyl β-methyl-Δ^{β}-pentenoate, b. p. 58—63°/14 mm. (13 g.). This was hydrolysed by refluxing with a solution of sodium hydroxide (8 g.) in water (30 c.c.) until a homogeneous solution was obtained (2 hours). After steam distillation and extraction with ether the residual alkaline liquor was acidified with dilute sulphuric acid and repeatedly extracted with ether. Distillation of the residue from the dried ether solution gave β-methyl-Δ^{β}-pentenoic acid, b. p. 102—103°/15 mm. (6·2 g.). This was converted through the acid chloride into its toluidide, m. p. 84° (Linstead, *J.*, 1927, 357), and its *anilide*, m. p. 97° after crystallisation from ligroin (Found: C, 76·3; H, 8·0; N, 7·7. $C_{12}H_{15}ON$ requires C, 76·3; H, 7·9; N, 7·4%).

FIG. 2.



NN'N''-Triphenylbiuret was prepared by the action of aniline on carbanilide in the presence of anhydrous stannic chloride. After crystallisation from methyl alcohol it had m. p. 151°, decomposing with gas evolution at 170—220°, resolidifying and again melting (as carbanilide) at 241°. This behaviour is very characteristic and is referred to throughout this paper as the " characteristic m. p. "

The apparatus used for the relatively large scale experiments is depicted in Fig. 1.

The apparatus was constructed in Pyrex glass, all joints being standard ground joints, painted externally with collodion after assembly. The central receiver, *G*, had four inlets, *a*, *b*, *c*, and *d*, arranged tetrahedrally, and a large bore tap exit, T_2, fitted with an internal ground joint into the neck of the reaction flask *R*. The receiver, *G*, was graduated in c.c. so that the quantity of reactants used could be ascertained. The inlets, *a*, *b*, and *c*, were connected to identical all-glass distillation systems, each distillation flask carrying a closed phosphorus pentoxide drying tube; the necessary rubber cork joints were coated externally with collodion. The main outlets, *d* and *T*, were connected through large phosphorus pentoxide drying tubes and the taps, T_3 and T_4, to a backing drying train and thence to the pump. Distillation flasks, *A* and *B*, were attached through an all-glass tap connection to the receiver of a Perkin triangle, itself attached to a similar Pyrex distillation system (not shown in Fig. 1) so that freshly distilled anhydrous stannic chloride or phenyl *iso*cyanate could be transferred into the flasks, *A* or *B*, respectively, without coming into contact with moisture.

Initially the whole apparatus was evacuated by means of an oil pump and heated strongly with a free flame to " degas " any water vapour adsorbed on the glass surfaces, and then left for 48 hours to complete the drying. The redistilled anhydrous stannic chloride was transferred from the Perkin receiver directly into the flask, *A*, which contained fresh phosphorus pentoxide. The tap, T_1, was then closed and the Perkin receiver was replaced by a glass stopper. Pure dry phenyl *iso*cyanate was similarly introduced through T_5 into *B* (also containing phosphorus pentoxide) from an identical distillation system. The pure sodium-dried olefin, contained in a tap-funnel, was then rapidly placed in flask *C* over fresh sodium and the whole apparatus was again left closed in contact with the various drying trains for one to two days.

The requisite quantities of the various reactants were then distilled (under reduced pressure) in turn into the central receiver, *G* (where their volumes were measured), and hence into the reaction flask, *R*. The flask, *R*, was then isolated from the rest of the apparatus by closure of the tap, T_2. In the case of volatile olefins the hydrocarbon was first distilled under ordinary pressure into the flask, *R*, which by suitable manipulation of the various taps was isolated from the rest of the apparatus during the distillation of the other reactants into the receiver, *G*, under reduced pressure.

At the end of the reaction period (usually 7—14 days) the flask, *R*, was connected at the joint, *r*, to a suitable distillation system and all volatile matter was distilled off in an oil-pump vacuum using a receiver cooled in liquid air. Remaining traces of phenyl *iso*cyanate and stannic chloride were removed from the reaction products in the flask, *R*, by prolonged evacuation. The condensed volatile products and the solid residue in the flask, *R*, were examined separately.

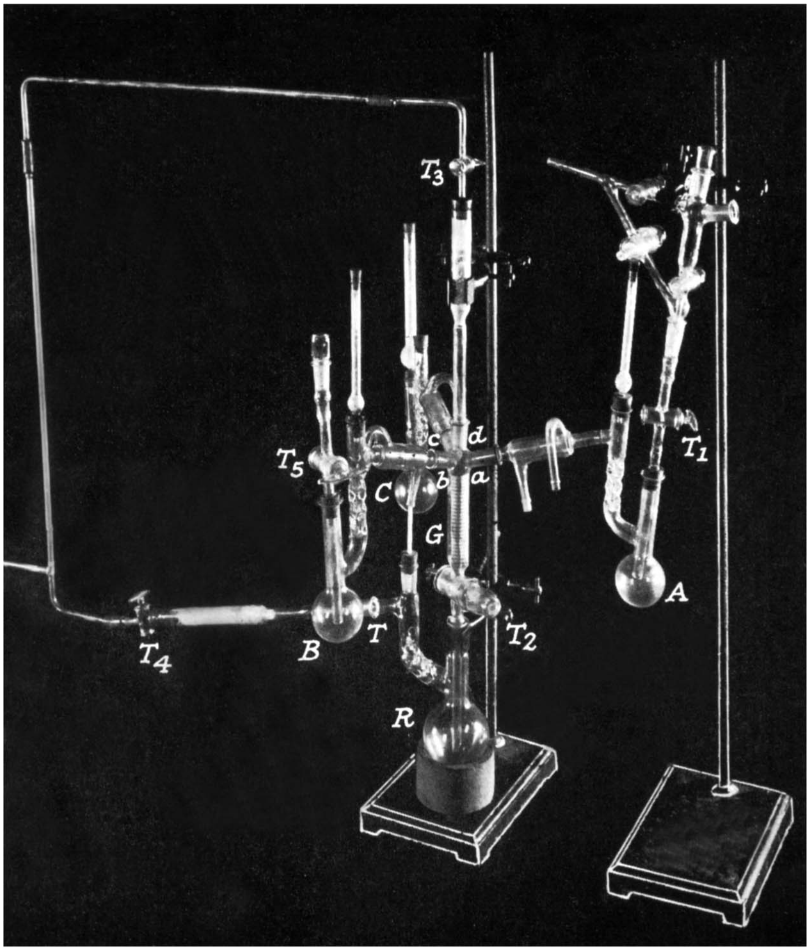
For smaller scale experiments a similar technique was employed, one, two or three sets of all glass distillation apparatus (B_1, B_2, B_3 respectively) being sealed to a common delivery tube attached to the reaction flask, R_1, which was itself sealed to a receiver of the type depicted in Fig. 2. After the various reaction materials had been distilled into the bulb, R_1, the apparatus was sealed off at S_1. After reaction the final volatile products were distilled into the bulb, R_2, which was then sealed off at S_2 for subsequent examination and the residue in R_1 was freed from remaining traces of phenyl *iso*cyanate and stannic chloride as above.

The majority of the experiments were carried out with trimethylethylene. The method of examination of the pro-

---

* All ligroin used in this work had b. p. 40—60°.

FIG. 1.



Apparatus used for the olefin–phenyl iso*cyanate–stannic chloride reaction with exclusion of moisture.*

[*To face p.* 728.

ducts varied slightly from experiment to experiment. In general, the volatile products (which contain a large excess of phenyl *iso*cyanate) were decomposed, with cold aqueous sodium carbonate, the bulk of the precipitated carbanilide and tin compounds were removed by filtration and the aqueous filtrate extracted with ether. From the residue obtained by evaporation of the dried ethereal solution some polymeric hydrocarbon fraction was isolated by extraction with cold ligroin.

The sticky solid, non-volatile reaction product (containing tin) was washed by decantation with cold ligroin to remove any last traces of unchanged phenyl *iso*cyanate, and the residue was extracted successively with boiling ligroin, ether and methyl alcohol. Any final insoluble residue was then decomposed with aqueous sodium carbonate (to remove tin) and the product was extracted with ether.

Reactions of Phenyl iso*Cyanate with Olefins.*—(1) *Trimethylethylene.* A large number of experiments using varying proportions of the olefin, phenyl *iso*cyanate and stannic chloride were performed and in each case a slightly different technique was necessary in order to isolate or identify the presence of triphenylbiuret in the product. In all cases the mixture of the three reactants, initially clear, developed crystal nuclei on the walls of the reaction vessel within 12—24 hours after mixing. During the following 24 hours a white skin of solid formed over all the walls of the vessel in contact with the mixture and the quantity of separated solid increased during the following few days. During the distillation of the volatile products (after 7—8 days), up to a bath temperature of *ca.* 50°/0·1 mm., considerable separation of solid occurred and the non-volatile residue was a sticky semi-solid yellowish-brown mass. After removal of traces of unchanged phenyl *iso*cyanate, by prolonged evacuation followed by washing with cold ligroin, this mass was repeatedly extracted with boiling ligroin. In the earlier experiments, in which no phosphorus pentoxide was introduced into the *liquid* phenyl *iso*cyanate and stannic chloride before the final distillation, evaporation of this ligroin extract sometimes gave very small amounts of triphenylbiuret, characteristic m. p. and mixed m. p. 150°, after recrystallisation from ether or methyl alcohol. Extraction of the insoluble residue with boiling ether gave some higher polymeric hydrocarbon and sometimes, a pale yellowish solid tin-complex (see below). Trituration of the ligroin–ether insoluble residue with small quantities of ice-cold methyl alcohol caused separation of triphenylbiuret in an almost pure condition. After removal of the methyl alcohol from the soluble portion the resulting brown gum was freed from tin by decomposition with cold aqueous 2N sodium carbonate and the products were extracted with ether. Attempted distillation of the residue from the dried ether solution caused decomposition with evolution of phenyl *iso*cyanate (identified by immediate reaction with aniline to give carbanilide, m. p. and mixed m. p. 241°) and carbanilide simultaneously crystallised from the material in the flask. The liquid thus still contained a considerable quantity of triphenylbiuret and this amount was approximately determined by isolating the carbanilide formed during the decomposition.

In the process of perfecting the technique for the complete exclusion of moisture, the final distillations of the phenyl *iso*cyanate and stannic chloride were effected with solid phosphorus pentoxide in the liquids. This technique seemed to increase greatly the quantity of less volatile (higher) polymerides of trimethylethylene formed and thus made it impossible to isolate solid triphenylbiuret as such from the very viscous non-volatile products (containing tin) or from the products obtained therefrom after decomposition with cold sodium carbonate solution to remove tin. The presence of considerable quantities of triphenylbiuret in these products was, however, established, and the quantity was approximately determined, by gentle distillation to effect decomposition. Phenyl *iso*cyanate (identified by conversion with dry ethyl alcohol into the urethane, m. p. and mixed m. p. 51°, or with aniline into carbanilide, m. p. and mixed m. p. 241°) distilled over and carbanilide (m. p. and mixed m. p.) separated in the distillation flask and was isolated and weighed.

In two experiments (Nos. 3 and 4) a considerable quantity of a pale yellowish-white solid tin-complex was isolated from the boiling ether extract of the non-volatile product (before decomposition with sodium carbonate, after removal) of polymeric hydrocarbon by trituration with benzene. This was repeatedly washed with ether, dried and analysed (Found: C, 28·5; H, 3·3; N, 5·2; Cl′, 35·2; Sn, 23·0. $C_{12}H_{14}N_2Cl_4Sn$ requires C, 32·2; H, 3·1; N, 6·3; Cl′, 31·8; Sn, 26·6%). It thus consists mainly of the solid aniline-stannic chloride *complex*, $2C_6H_5NH_2,SnCl_4$, and this was confirmed by its instant decomposition with effervescence by cold sodium carbonate solution to give aniline (extracted with ether), identified by conversion into benzanilide, m. p. and mixed m. p. 164°.

In experiment No. 5, the phenyl *iso*cyanate and stannic chloride were left in the reaction vessel, *R* (Fig. 1), without olefin for 7 days. No separation of solid occurred. The mixture was then completely distilled into a second reaction vessel, which had been originally built into the apparatus between *R* and the drying train. Only the merest trace of residue (0·05 g.), from which neither carbanilide nor triphenylbiuret could be isolated, remained in *R*. Trimethylethylene was then distilled into the redistilled mixture and the reaction now followed its normal course, 0·27 g. of triphenylbiuret being found in the products.

In one experiment the mixture of dry trimethylethylene with dry phenyl *iso*cyanate in *R* was left in contact with the *vapour* of dry stannic chloride from the distillation flask, *A* (Fig. 1). Little polymerisation of the olefin occurred but a small amount of triphenylbiuret (isolated as such, characteristic m. p. and mixed m. p. 150°) separated from the solution.

The data relating to the main large-scale experiments with trimethylethylene are summarised in the following Table:

	Wt. of reactants (g.).			Non-vol. residue (g.).	Triphenylbiuret (g.).		PhNCO recovered un-changed (g.).	% yield on PhNCO reacting.
Expt. No.	C_5H_{10}.	PhNCO.	$SnCl_4$.		(1) Isol.	(2) Det.		
1	12·9	21·6	36·2	14·8	0·77	0·53	14·0	16
2	10·0	16·9	4·5	4·25	0·10	>0·03	14·0	5
3 *	14·0	23·7	52·4	7·45	—	0·674	22·2	50
4 *	18·0	24·8	37·0	6·35	—	0·561	24·0	76
5 *	0	10·9	17·8	0·05	—	—	†	—

* PhNCO and $SnCl_4$ distilled over solid P_2O_5.

† Volatile distillate + C_5H_{10} gave 0·27 g. of triphenylbiuret (14%) and 8·8 g. of unchanged PhNCO.

(2) iso*Pentane.* The experiment was repeated using the identical apparatus and technique with phenyl *iso*cyanate (21·2 g.), stannic chloride (35·6 g.), and the corresponding saturated hydrocarbon, *iso*pentane, b. p. 28·6—28·9° * (13·3 g.), in place of the olefin, trimethylethylene. Unlike the experiments in which the olefin was used the mixture remained colourless and no trace of crystalline material had separated after 8 days. On distillation of the reaction mixture with a receiver cooled in liquid air the condensed volatile products (b. p. $\not>$ 40°/0·4 mm.) accounted for 97% by weight of the original reactants used. No solid separated during the distillation and only a minute trace of a brownish gum was left in the flask, probably originating from the small quantity of tap grease used to lubricate the wide-bore

---

* This specimen was kindly supplied by Messrs. Imperial Chemical Industries (Fertilizer and Synthetic Products) Ltd., Billingham. It was freed from any traces of unsaturated compounds by shaking with aqueous permanganate and was purified and dried by repeated fractional distillation over metallic sodium.

tap, T_2. This experiment proves that it is the olefin and not adventitious moisture which is responsible for the formation of the triphenylbiuret.

Interaction of trimethylethylene and phenyl iso*cyanate without catalyst.* Approximately 10 c.c. of dry trimethylethylene and 10 c.c. of dry phenyl *iso*cyanate were sealed together, without stannic chloride, using apparatus, B_2. The mixture remained quite clear and colourless for 6 days, after which period very minute traces of crystal nuclei could just be observed on the sides of the reaction vessel. After 7 days, distillation of the volatile products in the usual manner gave only 0·017 g. of residue, from which only 0·005 g. of carbanilide (m. p. and mixed m. p. 241°) was isolated, the remainder (0·012 g.) being, most probably, polymeric hydrocarbon. The volatile products consisted only of unchanged trimethylethylene and phenyl *iso*cyanate. This minute quantity of carbanilide almost certainly is a measure of the negligible traces of moisture which escape the rigorous drying technique and the experiment provides additional evidence that the formation of triphenylbiuret in the stannic chloride-catalysed reactions does not arise from the presence of adventitious moisture.

(3) *Tetramethylethylene.* This reaction was carried out in the apparatus shown in Fig. 1, using the technique previously described, with tetramethylethylene (5·6 g.), phenyl *iso*cyanate (8 g.) and stannic chloride (3·6 g.). The reactants formed a clear pale green solution which developed turbidity after three hours and crystal separation commenced after 6 hours. After 6 days at room temperature, volatile products (11·3 g.) were distilled off between 25—85°/0·7—0·4 mm. and condensed in a receiver cooled in liquid air. Decomposition of the distillate and the cold ligroin washings of the residue with cold, aqueous sodium carbonate gave carbanilide (6·25 g., corresponding to 7 g. of unreacted phenyl *iso*cyanate) together with a hydrocarbon fraction (0·85 g.) which was not examined. Extraction of the brown viscous residue in the reaction flask with boiling ether afforded crystalline material (0·7 g.) contaminated with gummy material from which *NN'N''*-triphenylbiuret was isolated. The cream-coloured powder (darkening from *ca.* 220° and not melting up to *ca.* 275°) (0·62 g.), insoluble in boiling ether, contained tin and was very soluble in methyl alcohol. It was decomposed with cold aqueous sodium carbonate and repeatedly extracted with ether. The residue from the dried ether extract partly crystallised and afforded more triphenylbiuret and a hydrocarbon oil (0·5 g.). The pure triphenylbiuret (0·16 g.), characteristic m. p. and mixed m. p. 149—150° after crystallisation from methyl alcohol, corresponded to a yield of 2·16% on the phenyl *iso*cyanate added or 17·2% when allowance is made for unreacted material.

(4) *Propylene.* A slightly modified technique was necessary for use with this gaseous olefin. The phenyl *iso*cyanate (14·7 g.) was distilled on to 4 g. of distilled stannic chloride contained in a thin sealed bulb in the reaction flask and the air was swept out by a current of propylene previously dried by passage through phosphorus pentoxide. The bulb of stannic chloride was broken and the flask again swept out with dry propylene. The flask exit tube was then closed and the whole reaction vessel was shaken mechanically, the propylene being maintained under slight pressure from a head of water in the gasometer. Over a period of about 634 hours (shaker stopped during nights) 3·05 litres (N.T.P.) of propylene were passed into the reaction flask. During the distillation of the volatile products of the reaction at 55°/12 mm., the exit tube became blocked with solid, hence their removal was completed in a vacuum desiccator over phosphorus pentoxide. It was therefore not possible to determine the amount of unreacted phenyl *iso*cyanate recovered in this experiment. The solid product in the reaction flask was extracted successively with dry boiling ligroin, ether, and methyl alcohol and from each of these extracts triphenylbiuret, characteristic m. p. 149—150°, was isolated. The final insoluble residue, containing tin, was decomposed with aqueous sodium carbonate, and extracted with ether. The ether solution yielded a further quantity of triphenylbiuret. The isolated triphenylbiuret (0·34 g.) corresponded to a 2·5% yield based on the total phenyl *iso*cyanate added to the reaction mixture.

(5) *aa-Diphenyl-Δ^{α}-propene,* cyclo*hexene* and *2-methyl-Δ^{1}-*cyclo*hexene.* Small scale experiments were carried out with these hydrocarbons and in each case small amounts of triphenylbiuret were isolated from the reaction products.

(6) cyclo*Pentadiene.*—Unless the mixture is well cooled throughout the slow addition of dry stannic chloride to a dry mixture of monomeric *cyclo*pentadiene, b. p. 41°, and phenyl *iso*cyanate, an uncontrollable reaction, accompanied by much charring and gas evolution, sets in leaving a carbonised product from which some carbanilide can be isolated by extraction with boiling ether. Under controlled conditions, using only a trace of stannic chloride, the main product is a very viscous liquid which, after removal of excess phenyl *iso*cyanate, consists mainly of a (nitrogen-free) rubbery polymeride which sets to a brittle glass. By dropwise addition of the dry olefin to the anhydrous stannic chloride–*iso*cyanate mixture at room temperature, the gaseous products formed over a period of 5—10 minutes were collected in a Hempel burette. A portion of the gas, collected over water, burned with the characteristic blue flame of carbon monoxide, and the remainder produced an immediate and heavy precipitate of black metallic silver when passed into the pyridine–silver oxide reagent at 50—60° (Manchot and Scherer, *loc. cit.*).

Olefinolysis of Unsaturated Anilides.—(1) *Vinylacetanilide.* In this series of experiments apparatus B_2 was used. The pure dry anilide (0·5 g.) was introduced into the reaction flask, R_1, before the unit was sealed on to the distillation system. The whole apparatus was then left in contact with the drying trains for a further 48 hours before the olefin and stannic chloride were introduced and again before they were distilled (from sodium and phosphorus pentoxide, respectively) on to the anilide. The apparatus was then completely sealed and left for four days. The receiver, R_2 (Fig. 2), was cooled in a freezing mixture and the gaseous products were aspirated through the pyridine–silver oxide reagent. A black precipitate of silver showed the formation of carbon monoxide. All volatile products were distilled under reduced pressure into the bulb, R_2, which was then sealed off at s_2. The non-volatile residue was a cream-coloured solid which was decomposed by breaking the bulb, R_1, and triturating under cold, 2N-sodium carbonate solution. After removal of insoluble tin compounds by filtration the filtrate was extracted with ether and the ether extract extracted twice with cold, dilute hydrochloric acid. This acid solution after diazotisation and coupling with β-naphthol gave a red dye, and it gave a precipitate of tribromoaniline with potassium bromate–bromide solution. Basification and ether extraction of the main bulk of the hydrochloric acid extract gave aniline (approx. 0·15 g.), identified by conversion into benzanilide, m. p. and mixed m. p. 164°. The experiment was repeated twice with similar results. Control experiments showed that no aniline is produced either by trituration of vinylacetanilide with cold aqueous sodium carbonate or by extraction of an ethereal solution of the anilide with cold, dilute hydrochloric acid.

From the dried ether extract of the sodium carbonate decomposition products of the volatile material, a small amount of a hydrocarbon fraction was isolated. This was ozonised, without purification, in ligroin solution for 24 hours. After removal of the solvent the oily ozonide was decomposed by boiling with water. No precipitate was produced in a solution of 2 : 4-dinitrophenylhydrazine in 2N hydrochloric acid attached to the top of the reflux condenser showing that no appreciable quantity of acetaldehyde was present (cf. p. 731). Distillation of the aqueous solution gave a faintly acid distillate which, after neutralisation, gave formaldehyde dimedon compound, m. p. and mixed m. p. 189°.

Similarly treated, the anilide of pyroterebic acid (0·45 g.) gave aniline (approx. 0·18 g.) (identified as benzanilide) together with an unsaturated hydrocarbon fraction; but β-methyl-Δ^{β}-penteno-anilide is much more resistant to fission, only ca. 10% olefinolysis occurring in six days (0·25 g. anilide afforded only 0·01 g. of aniline, identified as benzanilide). No olefinolysis was effected with either benzanilide or acetanilide (100% recovery of unchanged material), and pivalic anilide gave only the merest trace of aniline only detectable with the bromate–bromide reagent.

Vinylacetanilide–trimethylethylene alone. After vinylacetanilide (0·21 g.) had been left sealed (apparatus, B_1) for four days with sodium-dried trimethylethylene, evaporation of the olefin gave 0·21 g. of unchanged anilide.

Vinylacetanilide–phenyl iso*cyanate alone.* Vinylacetanilide (0·28 g.) was left sealed (apparatus, B_1) with phenyl *iso*cyanate for four days. The residue, after removal of volatile products, was a colourless oil which slowly crystallised after seeding with vinylacetanilide. The crude product (0·38 g.), m. p. 41—52°, was separated by repeated crystallisation from ether–ligroin into unchanged vinylacetanilide and, from the mother-liquor, *acetylmonovinylcarbanilide*, m. p. 84·5°, which depresses the m. p. of vinylacetanilide to 49° (Found: C, 74·1; H, 5·6; N, 10·4. $C_{17}H_{16}O_2N_2$ requires C, 74·3; H, 5·7; N, 10·0%). Prolonged boiling with dilute hydrochloric acid gave a strong odour of vinylacetic acid, and carbanilide, m. p. 235° raised to 237° by admixture with a genuine specimen, crystallised from the aqueous liquor.

Formation and Reactions of Stannic Chloride Complexes.—The preparation of the various stannic chloride complexes was carried out either in apparatus B_1 or B_2 according as to whether the second component was a solid or a liquid. Rigid exclusion of moisture was effected by the technique described for the olefin experiments. After reaction, all excess of volatile materials was distilled off, the last traces being removed in a high vacuum. The solid complex was repeatedly washed with sodium-dried ligroin and (when stable) ether and stored in a vacuum desiccator over phosphorus pentoxide.

(1) *Aniline.* When mixed at room temperature freshly distilled dry aniline and anhydrous stannic chloride react readily, with considerable evolution of heat, to form a clean white solid *complex.* The complex was shown to be free from uncombined aniline by digestion with ether, but was readily decomposed by cold sodium carbonate solution with effervescence to yield free aniline. The composition of the complex was determined by hydrolysis with boiling hydrochloric acid (1 : 1) and determination of the aniline in the acid solution by titration with a standard potassium bromate–bromide solution. Chloride ion was determined by hydrolysis with boiling sodium carbonate solution, removal of the liberated aniline by steam distillation and titration of chloride ion in the neutralised solution with standard silver nitrate (potassium chromate as indicator). Tin was determined gravimetrically as SnO_2 after precipitation as its sulphide (Found: $C_6H_5NH_2$, 41·75; Cl′, 31·25; Sn, 22·4. $2C_6H_5NH_2,SnCl_4$ requires $C_6H_5NH_2$, 41·6; Cl′, 31·8; Sn, 26·6%).

(2) *Carbanilide.* Pure carbanilide was similarly sealed with anhydrous stannic chloride for several hours. A uniform white emulsion was formed. After removal of excess of stannic chloride the *complex* was well washed with dry ligroin and stored in a vacuum desiccator over phosphorus pentoxide (Found: Cl′, 25·1; Sn, 20·1. $3[CO(NHC_6H_5)_2],2SnCl_4$ requires Cl′, 24·5; Sn, 20·5%). The complex darkens at 190—200° and has m. p. 215—220° (decomp.). It is slightly soluble in boiling ether and is recovered unchanged after evaporation of the solvent. Crystallisation from boiling methyl alcohol causes decomposition, and carbanilide, m. p. 241°, crystallises from the solution on cooling. A complex with similar characteristics was isolated in the products of the reaction between phenyl *iso*cyanate and trimethylethylene in the presence of stannic chloride.

(3) *Vinylacetanilide.* Similarly prepared the *complex* from vinylacetanilide and anhydrous stannic chloride is a viscous liquid which sets to a glass, readily broken up into a friable powder which is very hygroscopic. This complex seems to be much less stable than the others. After repeated trituration and washing with cold dry ligroin and drying over phosphorus pentoxide, the complex was analysed by hydrolysis with concentrated hydrochloric acid for 1·5 hours and titration of the aniline with potassium bromate–bromide solution. Chloride ion was determined by heating the complex with 0·1N silver nitrate (20·0 c.c.) and a few c.c. of fuming nitric acid on a steam bath for 1·5 hours and determination of the excess silver nitrate with a standard solution of ammonium thiocyanate (Found: $C_6H_5NH_2$, 21·2; Cl′, 31·0. $C_3H_5{\cdot}CO{\cdot}NHC_6H_5,SnCl_4$ requires $C_6H_5NH_2$, 22·0; Cl′, 33·8%). The complex, decomposed by trituration with cold sodium carbonate solution, and extraction of the liquors with ether, gave vinylacetanilide, m. p. and mixed m. p. 61°.

NN′N″-Triphenylbiuret was recovered unchanged after it had been left sealed with anhydrous stannic chloride for several weeks.

Reaction of Aniline–Stannic Chloride Complex with Phenyl iso*Cyanate.*—The complex, free from uncombined aniline, was sealed with an excess of phenyl *iso*cyanate using apparatus, B_1, and the usual technique. After several days a uniform white emulsion formed which left a clean white solid after removal of all volatile matter in the usual way. Extraction of this solid with boiling ligroin afforded *NN′N′*-triphenylbiuret, characteristic m. p. 151° after crystallisation from methyl alcohol. The boiling ether extract of the ligroin-insoluble portion deposited crystals of carbanilide, m. p. 241°, and a further quantity of the biuret was obtained from the ethereal mother liquor. Crystallisation of the ligroin–ether-insoluble residue, which contains tin, from boiling methyl alcohol afforded more carbanilide.

Reaction of the Carbanilide–Stannic Chloride Complex with Phenyl iso*Cyanate.*—The complex (1·47 g.) was sealed with an excess of phenyl *iso*cyanate, using apparatus, B_1; immediate reaction occurred with evolution of heat. The mixture was kept at room temperature for 2 days. Evaporation of the volatile products (excess phenyl *iso*cyanate and stannic chloride only) left a white solid (1·25 g.) which, after two crystallisations from methyl alcohol, gave pure *NN′N″*-triphenylbiuret (1·15 g.), characteristic m. p. 150—151°, in 91% yield.

Attempted Electrolysis of a Trimethylethylene–Stannic Chloride Mixture.—An all-glass electrolytic cell, suitably constructed so that any gaseous products could be collected and investigated, was connected by means of a side-arm carrying a standard glass joint to the reaction flask, *R*, of apparatus in Fig. 1 and a few c.c. each of dry trimethylethylene and anhydrous stannic chloride were distilled into the cell under the usual conditions for the rigid exclusion of moisture. The cell was sealed off at the side arm before detachment from the apparatus, and a D.C. voltage of 110 volts was applied across the platinum electrodes. No trace of current was detectable on a microammeter placed in the circuit, either immediately after mixing the reactants or after they had been left in contact for 24 hours. An approximate estimation of the resistance of the liquid column showd that it was at least 10^7 ohms.

Polymeric Hydrocarbon Products.—Fractional distillation of the polymeric hydrocarbon fractions of the various trimethylethylene experiments (isolated as described on p. 729) gave three distinct fractions: (1) b. p. 55—65/15 mm., (2) b. p. 109—114°/14 mm., (3) b. p 104—110°/0·6 mm. After redistillation over sodium the following analytical figures were obtained [Found: (1) C, 85·4; H, 14·35. (2) C, 85·1; H, 14·1. (3) C, 85·15; H, 13·6. Calc. for C_nH_{2n}: C, 85·7; H, 14·3%].

Structure of fraction (1). The most volatile hydrocarbon fraction was ozonised in solution in ligroin at 0°. The gaseous product obtained when the resulting ozonide was decomposed with boiling water was proved to be acetaldehyde by precipitation of its 2 : 4-dinitrophenylhydrazone (isolated in two forms, m. p. 161° and 147°, both raised to m. p. 164—165° by admixture with a genuine specimen).

Distillation of the residual aqueous liquor gave an aqueous distillate having a camphoraceous odour; from this, after extraction with ether, the dimedon compound of acetaldehyde, m. p. and mixed m. p. 137—138°, was obtained. The ether extract of the aqueous distillate gave a very small amount of a camphoraceous oil which was converted into a *semicarbazone*, m. p. 159°, after crystallisation from dry ether (Found: C, 58·6; H, 10·1. $C_9H_{19}ON_3$ requires C, 58·4; H, 10·3%). Admixture with the semicarbazone, m. p. 173°, or δδ-dimethyl-*n*-hexan-β-one (below) raised the m. p. to 168° (previous softening).

*Synthesis of δδ-Dimethyl-*n*-hexan-β-one.*—Fractional distillation of the product obtained by the action of *tert.*-amyl bromide (31 g.) on ethyl acetoacetate (26 g.) in ethyl alcohol (70 c.c.) in which sodium (4·6 g.) had been dissolved, gave mainly a very volatile product, b. p. <40°/20—30 mm., unchanged ethyl acetoacetate, and only about 1 g. of *ethyl* tert.*-amylacetoacetate*, b. p. 104°/9 mm. (Found : C, 65·6; H, 10·0. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·1%). Its *semicarbazone*, prepared in the usual manner, had m. p. 110°, after crystallisation from ether–ligroin (Found : C, 55·7; H, 9·0; N, 15·9. $C_{12}H_{23}O_3N_3$ requires C, 56·0; H, 9·1; N, 16·3%).

The small amount of ketonic ester was hydrolysed by boiling under reflux with concentrated hydrochloric acid for 24 hours followed by keeping for 3 days at room temperature. Distillation of the hydrolysate gave an aqueous distillate with a strong camphoraceous odour. This was saturated with sodium acetate and the ketone was converted, without isolation, into its *semicarbazone*, m. p. 173° (165° on re-melting; cf. above), after crystallisation from dry ether (Found : N, 22·8. $C_9H_{19}ON_3$ requires N, 22·7%).

We thank Imperial Chemical Industries Limited, Dyestuffs Division, for facilities which have enabled this work to be carried out.

THE UNIVERSITY, LEEDS.

[*Received, June* 11*th*, 1945.]