374. *Short-chain Polymerisation of Styrene in Presence of Stannic Chloride and Hydrogen Chloride.*

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Hydrogen chloride inhibits the long-chain polymerisation of styrene, catalysed by stannic chloride. Styrene reacts with hydrogen chloride, in presence of stannic chloride, in carbon tetrachloride medium, to form 1-phenylethyl chloride and di-, tri-, tetra- and penta-styrenes, all of which have been isolated. The polymers are formed in increasing proportions as the initial concentration of styrene is raised. Ozonisation shows them to have the structure $CHPh{:}CH{\cdot}[CHPh{\cdot}CH_2]_n{\cdot}CHPh{\cdot}CH_3$. Distyrene does not react with hydrogen chloride and stannic chloride; but 1-phenylethyl chloride reacts (in presence of stannic chloride) with styrene and, more slowly, with distyrene to form polymers. The reactions are consistent with a mechanism in which a proton, derived from the interaction of hydrogen chloride with stannic chloride, attaches itself to the styrene molecule, forming a carbonium ion, which may form 1-phenylethyl chloride reversibly, or may grow by accretion of monomeric styrene until stabilised to form the short-chain polymers. Distyrene is accompanied by a saturated isomer, possibly an indane derivative, which may be formed by cyclisation of the carbonium ion.

In carbon tetrachloride solution, in presence of stannic chloride, styrene polymerises to form polymers of molecular weight 1500—3000 (cf., *e.g.*, Williams, *J.*, 1940, 775). Traces of hydrogen chloride can inhibit polymerisation temporarily but completely (Williams, *Nature*, 1937, **140**, 363), hydrogen chloride being consumed while acting as inhibitor. When a continuous supply of hydrogen chloride is led into a carbon tetrachloride solution of styrene and stannic chloride, there is no long-chain polymerisation; instead, 1-phenylethyl chloride, distyrene, and "short-chain polystyrene" are formed, in proportions which depend upon the initial concentration of styrene (Williams, *J.*, 1938, 1046). To support a kinetic study (now in progress), we have re-examined the products of this reaction; and new experiments, described in this paper, have proved the "short-chain polystyrene" to be mainly tristyrene and tetrastyrene, with some pentastyrene. Experiments covering a range of initial styrene concentrations have determined the extent to which the proportions of the reaction products may vary. In these experiments, shown in Tables I and II, dry hydrogen choride was led into solutions of styrene and stannic chloride in carbon tetrachloride at 20—25°, until the whole of the styrene had been consumed, as indicated by titration of the residual styrene with bromine (Williams, *J.*, 1938, 246). (In some experiments, at the higher styrene concentrations, the reactions were continued for times—enclosed in parentheses in the tables—which were much longer than those required for complete consumption of the original styrene.)

At the lowest styrene concentrations, a maximum of 75% of styrene is recovered as 1-phenylethyl chloride, whose structure follows from its conversion into 2 : 3-diphenylbutane. This is the normal product of addition of hydrogen chloride to the styrene double bond (Schramm, *Ber.*, 1893, **26**, 1709; cf. Walling, Kharasch, and Mayo, *J. Amer. Chem. Soc.*, 1939, **61**, 2693, for the analogous hydrogen bromide addition).

The proportion of 1-phenylethyl chloride in the product falls with rising initial concentration of styrene; and the yield of distyrene appears to reach a maximum of 40% at about 2·5M-styrene (Expts. 13, 20, 24). The yields of the products called in Table I "short-chain polystyrene" increase at still higher styrene concentrations (*e.g.*, in Expts. 37 and 38). The short-chain polystyrene consists mainly of tri-, tetra-, and penta-styrenes, all of which can be distilled at pressures of 1 mm.; but it also contains a certain proportion of polymer, with higher molecular weight, which does not distil under the conditions employed. Expt. 38, carried out with 30 g. of styrene at 5·3M-concentration, shows that the amount of non-distillable polymer formed does not exceed 8% of the initial styrene; and it may be supposed that non-distillable polymer is formed in smaller proportions at lower styrene concentrations. However, in experiments performed with smaller initial amounts of styrene, the attempted quantitative separation of distillable from non-distillable polymer tends to exaggerate the latter (*e.g.*, in Expt. 37). Only at the highest styrene concentrations employed does the non-distillable polymer residue contain polystyrene of high enough molecular weight to be capable of precipitation in methyl alcohol. The mean (cryoscopic) molecular weight of a non-distillable residue from 4M-initial styrene was 633. The non-distillable residue from 5·3M-styrene contained 3·8% of the initial styrene as polymer, with mean molecular weight 881, which was precipitated by methyl alcohol. These molecular weights are much smaller than those (up to 3,000) obtained at comparable styrene concentrations in the absence of hydrogen chloride.

It should be noted that, in experiments of long duration (*e.g.*, cf. Expts. 24 and 20 of Table II), the yields of individual products may have been affected by interaction between 1-phenylethyl chloride and distyrene (cf. Table III) after the initial styrene had been used up.

TABLE I.

Interaction of styrene with hydrogen chloride and stannic chloride. Solvent : Carbon tetrachloride. Temp. : 20—25°. *Dry hydrogen chloride led through solutions.* (*Concn. of* HCl : 0·14M.)

				% Styrene recovered as :			
Expt. no.	Styrene concn., M.	$SnCl_4$ concn., M.	Time, mins.	C_8H_9Cl.	$C_{16}H_{16}$.	Short-chain polystyrene.	Total yield, %.
10	0·08	0·044	180	73·9	←------- 11 -------→		84·9
11	0·08	0·044	187	74·0	←------- 20·1 -------→		94·1
9	0·17	0·026	172	75·0	15·0	3·9	93·9
6	0·17	0·035	210	64·0	7·3	9·9	81·2
7	0·17	0·044	186	69·0	7·1	5·5	81·6
1	1·11	0·022	183	58·0	7·9	14·0	79·9
4	1·73	0·044	(150)	38·0	←------- 54·0 -------→		92·0
14	1·73	0·088	(182)	50·5	31·7	16·1	98·3
13	2·5	0·088	(180)	22·1	40·2	33·9	96·2
5	3·4	0·088	(175)	8·5	12·0	66·0	86·5
12	3·4	0·088	(180)	2·4	29·1	57·2	88·7
37	4·0	0·088	10	11·1	31·3	54·5 *	96·9
38	5·3	0·088	12	7·4	27·4	59·2 †	94·0
3	5·3	0·088	(180)	2·0	9·0	59·0 ‡	70·0
31 §	1·73	0·044	(90)	21·1	37·4	23·0	81·5
30 §	2·5	0·088	(105)	6·2	9·0	50·4	65·6

* Containing at least 23·5% of the initial styrene as tri- and tetra-styrenes.

† Short-chain polystyrene composed of 24·0% of initial styrene as fraction with b. p. 185—300°/12 mm. (mainly tristyrene); 27·3% as fraction with b. p. 300—360°/12 mm. (mainly tetra- and penta-styrenes); and 7·9% as distillation residue.

‡ 3·8% of styrene recovered as polymer insoluble in methyl alcohol.

§ At 76°.

Structures of the Polymers.—The distyrene has already been identified (*J.*, 1938, 1046) as the one prepared by Erlenmeyer (*Annalen*, 1865, **135**, 122), by Fittig and Erdmann (*ibid.*, 1883, **216**, 179), by Stoermer and Kootz (*Ber.*, 1928, **61**, 2330), and by Risi and Gauvin (*Canadian J. Res.*, 1936, *B*, **14**, 255). Stobbe and Posnjak (*Annalen*, 1909, **371**, 287) proved it to be 1 : 3-diphenylbut-1-ene (I) (see p. 1870). The identification of the distyrene of Table I with this compound is still further strengthened in the experimental section. When isolated as a product of the reaction of styrene with hydrogen chloride and stannic chloride, this distyrene is, however, accompanied by a saturated isomer (see next paragraph).

The tristyrene and tetrastyrene isolated from experiments with high initial styrene concentrations both give benzaldehyde on ozonisation. It therefore seems probable that they are, respectively, 1 : 3 : 5-triphenylhex-1-ene (III) and 1 : 3 : 5 : 7-tetraphenyloct-1-ene (IV). It may be recalled that Stoermer and Kootz (*loc. cit.*) obtained benzaldehyde and hydratropic aldehyde by ozonisation of distyrene of structure (I), whereas Staudinger and Steinhofer (*Annalen*, 1935, **517**, 35) obtained no analogous products by oxidation of the differently constituted di- and tri-styrenes isolated from the products of pyrolysis of long-chain polystyrene.

Some pentastyrene was isolated by distillation of the combined polymer products of several experiments. There is no reason against supposing that its structure is analogous to those of the smaller polymers.

Saturated Distyrene.—When isolated from the reaction mixture, the distyrene is usually found to be heavily contaminated with a saturated isomer. Table II shows the extent of unsaturation of the distyrene in a number of experiments, as determined by addition of iodine chloride or bromine to the double bond. Formation of distyrene dibromide from the partially saturated material, followed by regeneration of the olefin by the action of zinc, gave distyrene 99·5—100% unsaturated, as estimated by the same procedure, always supposing the molecule to contain one double bond.

The formation of the saturated distyrene is not surprising, because stannic chloride is known to catalyse the conversion of the unsaturated distyrene (I) into a saturated isomer (Risi and Gauvin, *loc. cit.*). The structure of the saturated dimer has not been proved. By analogy with the known structures of the saturated dimers of 1-methylstyrene and 1 : 1-diphenylethylene (Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1930, **52**, 4021; Bergmann and Weiss, *Annalen*, 1930, **480**, 49; Bergmann, Taubadel, and Weiss, *Ber.*, 1931, **64**, 1493) the saturated

TABLE II.

Extent of unsaturation of distyrene.

Expt. no.	Initial styrene, M.	$SnCl_4$, M.	Time, mins.	% Styrene recovered as :		% Unsaturation of $C_{16}H_{16}$.
				C_8H_9Cl.	$C_{16}H_{16}$.	
28	1·73	0·085	28	31	30	27·7
25	1·89	0·048	45	45·1	12	47
27	1·89	0·048	33	30·5	26·4	38
29	2·02	0·021	71	29·2	19·1	36
26	2·31	0·044	46	39·5	28	31
23	2·5	0·04	25	24	31	20
24	2·5	0·04	15	33	37	20
20	2·5	0·04	(120)	13	37	76
22	2·5	0·04	(120)	14	36	23

distyrene has been supposed (Risi and Gauvin, *loc. cit.*; Stanley, *Chem. and Ind.*, **1939**, **58**, 1080) to be 1-phenyl-3-methylindane (II), contrary to the opinion of Stoermer and Kootz (*loc. cit.*), who thought that the isomer was unsaturated.

In the absence of a catalyst, the isomerisation of distyrene is not at all rapid; distyrene from a reaction product, initially 96% unsaturated, was still 94% unsaturated when retested after standing in daylight for 19 days.. The conversion of distyrene, initially 100% unsaturated, into the saturated isomer in presence of stannic chloride is shown in Expts. 35 and 36 of Table III.

A specimen of tristyrene, isolated from the reaction products, gave a halogen absorption (in 75 mins.) corresponding to 68·5% unsaturation; but halogen absorption is slow and is not a very certain method for the quantitative estimation of unsaturation in polystyrenes (cf. Staudinger and Steinhofer, *loc. cit.*). On the other hand, the formation of 1-phenyl-3-(2′-phenyl-*n*-propyl)indane from tristyrene (III) is not impossible; and Risi and Gauvin (*loc. cit.*) have suggested that this kind of cyclisation may be a possible chain-termination process in the long-chain polymerisation of styrene.

Mechanism of the Reaction.—The products listed in Tables I and II can react further among themselves. This is shown by the results given in Table III. Experiments described in an earlier paper (*J.*, 1938, 1046) have already proved :

(1) that styrene and hydrogen chloride do not react together in the absence of a catalyst;

(2) that racemic 1-phenylethyl chloride does not undergo any substantial change under the influence of stannic chloride, 90% of the original material being recovered unchanged after contact for 140 mins. in carbon tetrachloride medium.

The results of Table III show :

(3) that distyrene does not change appreciably under the combined action of hydrogen chloride and stannic chloride, except for a slow conversion to its saturated isomer (Expts. 15, 35, 36);

(4) but that 1-phenylethyl chloride reacts with styrene (Expts. 32, VIII) and, more slowly, with distyrene (Expt. 33) to form polymers. This is particularly evident from the

TABLE III.

Further interactions of products.

Current of hydrogen chloride passed only in Expts. 15, 35, 36.

Expt. no.	Starting materials.	$SnCl_4$ concn., M.	Time, mins.	% Styrene recovered as :				Total yield.
				C_8H_9Cl.	$C_{16}H_{16}$.	$(C_8H_8)_{3-4}$.	Non-dist. polymer.	
15	$C_{16}H_{16}$* : 0·89M	0·088	180	0	92·2	0	4	96·2
35	$C_{16}H_{16}$† : 0·53M	0·047	75	0	91·0‖			91·0
36	$C_{16}H_{16}$‡ : 2·06M	0·047	75	0	90·0¶			90·0
32§	C_8H_8 : 1·81M (0·079) C_8H_9Cl : 0·92M (0·040)	0·080	92	2·1 (0·0026)	41·6 (0·050)	30·7 (0·037)	17·3 (0·024)	91·7
VIII§	C_8H_8 : 1·7M (0·14) C_8H_9Cl : 0·75M (0·060)	0·086	1500	0	20 (0·050)	←------- 66 -------→ (0·16)		86
33§	$C_{16}H_{16}$† : 0·87M (0·073) C_8H_9Cl : 0·75M (0·030)	0·080	385	16·4 (0·017)	53·0 (0·055)	19·8 (0·020)	2·5 (0·0026)	91·7

* Partly saturated.

† 100% unsaturated.

‡ 95·5% unsaturated.

‖ 95% unsaturated.

¶ 87% unsaturated

§ Moles of starting materials corrected for amounts of solution extracted for analysis. Yields calculated on total C_8H_8 in combined C_8H_8 and C_8H_9Cl. Moles of polystyrene always given as moles of C_8H_8 in given weight of polymer. Experiment VIII taken from *J.*, 1938, 1046.

numbers of moles of starting materials and end products, given in parentheses for the relevant experiments in Table III. In the long experiment VIII, the 1-phenylethyl chloride is completely consumed.

The following suggested interpretation of the reactions is based upon the evidence which exists that an alkyl halide and a metal halide catalyst form a complex which is ionised, though not necessarily much *dissociated* into free ions in a solvent of low dielectric constant (cf., *e.g.*, Fairbrother, *Trans. Faraday Soc.*, 1941, **37**, 763; Price, *Chem. Reviews*, 1941, **29**, 37). The free ions represented in the equations would perhaps be more properly visualised as ion pairs, themselves existing, in a carbon tetrachloride medium, in small concentration only (Fairbrother, *J.*, 1945, 503).

" Normal " polymerisation :

$$\mathrm{CHPh{:}CH_2 + SnCl_4 \rightleftharpoons \overset{+}{C}HPh{\cdot}CH_2{\cdot}\overset{-}{S}nCl_4} \quad \ldots\ldots \quad (1)$$

$$\mathrm{CHPh{:}CH_2 + \overset{+}{C}HPh{\cdot}CH_2{\cdot}\overset{-}{S}nCl_4 = \overset{+}{C}HPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}\overset{-}{S}nCl_4,\ etc.} \quad \ldots\ldots \quad (2)$$

In presence of hydrogen chloride :

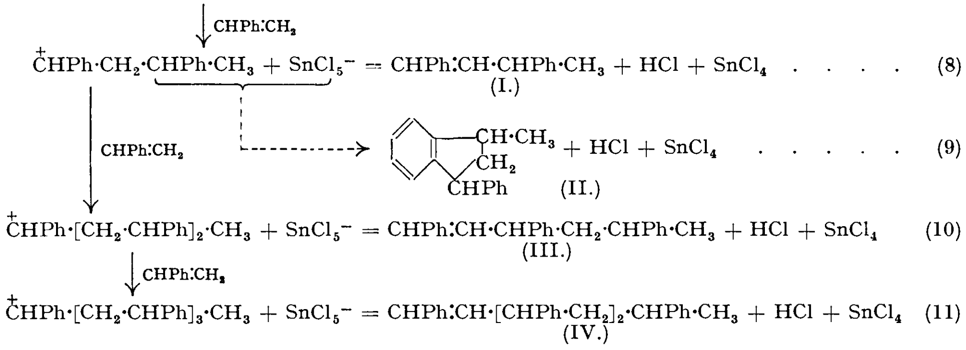
$$\mathrm{HCl + SnCl_4 \rightleftharpoons H^+ + SnCl_5^-} \quad \ldots\ldots \quad (3)$$

$$\mathrm{CHPh{:}CH_2 + H^+ = \overset{+}{C}HPh{\cdot}CH_3} \quad \ldots\ldots \quad (4)$$

$$\mathrm{\overset{+}{C}HPh{\cdot}CH_2{\cdot}\overset{-}{S}nCl_4 + H^+ = \overset{+}{C}HPh{\cdot}CH_3 + SnCl_4} \quad \ldots\ldots \quad (5)$$

$$\mathrm{\overset{+}{C}HPh{\cdot}CH_3 + HCl = CHPhCl{\cdot}CH_3 + H^+} \quad \ldots\ldots \quad (6)$$

$$\mathrm{\overset{+}{C}HPh{\cdot}CH_3 + SnCl_5^- \rightleftharpoons CHPhCl{\cdot}CH_3 + SnCl_4} \quad \ldots\ldots \quad (7)$$



$$\mathrm{\overset{+}{C}HPh{\cdot}CH_3 \xrightarrow{CHPh{:}CH_2} \overset{+}{C}HPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH_3}$$

$$\mathrm{\overset{+}{C}HPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH_3 + SnCl_5^- = \underset{(I.)}{CHPh{:}CH{\cdot}CHPh{\cdot}CH_3} + HCl + SnCl_4} \quad \ldots \quad (8)$$

$$\mathrm{\cdots\cdots \rightarrow (II.) + HCl + SnCl_4} \quad \ldots \quad (9)$$

$$\mathrm{\overset{+}{C}HPh{\cdot}[CH_2{\cdot}CHPh]_2{\cdot}CH_3 + SnCl_5^- = \underset{(III.)}{CHPh{:}CH{\cdot}CHPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH_3} + HCl + SnCl_4} \quad (10)$$

$$\mathrm{\Big\downarrow CHPh{:}CH_2}$$

$$\mathrm{\overset{+}{C}HPh{\cdot}[CH_2{\cdot}CHPh]_3{\cdot}CH_3 + SnCl_5^- = \underset{(IV.)}{CHPh{:}CH{\cdot}[CHPh{\cdot}CH_2]_2{\cdot}CHPh{\cdot}CH_3} + HCl + SnCl_4} \quad (11)$$

In the absence of hydrogen chloride, stannic chloride catalyses the polymerisation of styrene to relatively long-chain products, *e.g.*, with 1·7M-initial styrene, to molecules of the order $(C_8H_8)_{23}$.

If catalysts of the " Friedel–Crafts " type initiate polymerisation by polarising the olefinic double bond (cf., *e.g.*, Price, *Ann. New York Acad. Sci.*, 1943, **44**, 351; Hulburt, Harman, Tobolsky, and Eyring, *ibid.*, p. 371), the " normal " polymerisation may be propagated by processes of the type shown in equations (1) and (2). The presence of hydrogen chloride prevents the " normal " polymerisation: with 1·7M-styrene in presence of stannic chloride and 0·14M-hydrogen chloride, none of the material formed can be precipitated in methyl alcohol, and the largest polymer isolated is $(C_8H_8)_{3-4}$, in about 16% yield (Table I, expt. 14). The reaction in presence of hydrogen chloride is also faster than the " normal " polymerisation in its absence. This is shown in Table IV, which contains results taken from previous work on the " normal " polymerisation (cf. *J.*, 1940, 775), together with figures from Tables I and II, above.

TABLE IV.

Stannic chloride : 0·04—0·05M

Concn. C_8H_8, M	0·17	0·35	0·86	1·7	1·9	2·5	3·5	4·0
" Normal " polymerisation in absence of hydrogen chloride.								
% Consumption of C_8H_8	—	46	50	61	—	—	84	—
Time, mins.	—	5400	1600	190	—	—	162	—
Reaction with 0·14M-HCl; complete consumption of styrene in :								
Time, mins.	186	—	—	—	33	15	—	10

It follows that the formation of the products shown in Tables I and II cannot be due to the interruption of " normal " polymerisation chains, since the latter are initiated too slowly to account for the formation of these products within the times observed. Hydrogen chloride and stannic chloride in combination must act in two ways : (*a*) in stopping the " normal " polymerisation chains, and (*b*) in propagating much shorter chains by a different mechanism. The polymerisation complex of equation (1) must either be decomposed into styrene by hydrogen chloride; or it must be diverted by hydrogen chloride into an alternative path (equation 5).

The combined catalytic action of hydrogen chloride and stannic chloride in carbon tetrachloride resembles the catalytic action of aqueous sulphuric or hydrochloric acid upon styrene (Risi and Gauvin, *loc. cit.*) in producing small polymers only. In the presence of stannic chloride, therefore, the catalytic behaviour of hydrogen chloride is similar to that of a strong acid. By analogy with the influence exerted by Friedel–Crafts catalysts upon alkyl halides, it seems probable that hydrogen chloride and stannic chloride will react, in carbon tetrachloride, as shown in equation (3). (Alternatively, $SnCl_6^{--}$ may be formed.) Evidence for some such interaction may be seen in Meerwein's observation (*Annalen*, 1927, **453**, 16) that dilute ethereal solutions of hydrogen chloride and of stannic chloride are, separately, *yellow* after addition of the indicator *p*-dimethylaminoazobenzene; but that an immediate *red* colour is formed as soon as the two yellow solutions are mixed. The virtually free proton from (3) may react with styrene, as in (4), or may decompose the " normal " polymerisation complex, as in (5), forming, in either event, a carbonium ion, which can be converted into 1-phenylethyl chloride by (7), and perhaps also by (6). The reaction (7) must be supposed reversible to account for Bodendorf and Böhme's discovery (*Annalen*, 1935, **516**, 1) that optically active 1-phenylethyl chloride is racemised by the action of stannic chloride (interpreted by these authors by equations equivalent to 7); and also to account for the reactions of 1-phenylethyl chloride with styrene and distyrene (Table III). (Cf., also, the elimination equilibrium discussed by Hughes, Ingold, and Scott, *J.*, 1937, 1271.) The formation of the polystyrenes (I), (III), and (IV) is represented by the addition of monomeric styrene to a carbonium ion of increasing chain length, coupled with the stabilisation processes, typified by (8), which are evidently more efficient than the chain-termination processes occurring in the normal polymerisation in absence of hydrogen chloride. The stabilisation reactions are not reversible; because distyrene does not polymerise further in the presence of hydrogen chloride and stannic chloride (Table III), though it does undergo slow isomerisation into its saturated isomer (II). In view of the slowness of this isomerisation (Table III, expts. 35, 36), it seems doubtful whether the substantial amounts of saturated distyrene in the reaction products can be formed by direct isomerisation within the times observed (Table II, expts. 23—29). It is more probable that the saturated distyrene (II) is produced by cyclisation of the carbonium ion, through attack by the positive end of the ion upon the benzene ring, with elimination of a proton (equation 9).

Whether styrene *must* be in the form of a complex with the catalyst in order to take up a proton, as in (5), cannot be certain; but equation (4) seems to represent a likely reaction. The general question, whether the hydrocarbon component in a Friedel–Crafts alkylation needs to be activated by association with the catalyst, has been raised by Ingold (*Trans. Faraday Soc.*, 1941, **37**, 769).

EXPERIMENTAL.

Materials.—Pure commercial styrene, stabilised with quinol, was redistilled before use. The stannic chloride was obtained from early fractions taken off during the distillation (in a vacuum) of stannic chloride prepared from tin and chlorine. The reaction medium was AnalaR carbon tetrachloride, dried before use. Distyrene (I) was made in quantity (cf. Risi and Gauvin, *loc. cit.*) by refluxing styrene (90 g.) for 8 hours with concentrated sulphuric acid (59 g.) and water (48 g.). The preparations gave 82% yields of distyrene, 67—79% unsaturated, from which the dibromide was prepared (in acetic acid). The action of zinc upon the dibromide gave up to 76% yield of distyrene, 99·5—100% unsaturated.

The reactions referred to in Tables I and II were carried out by leading a stream of dry hydrogen chloride through solutions of styrene (10—30 g.) and stannic chloride in carbon tetrachloride at 20—25°. When all the styrene had been consumed, the reaction products were isolated as described previously (1938), by washing the reaction mixture with water, drying and separating into fractions by distillation under reduced pressure.

Identification of Reaction Products.—The following products were isolated. (Molecular weights were determined cryoscopically in benzene solution. Analyses are by Drs. Weiler and Strauss, Oxford.)

(1) 1-Phenylethyl chloride, b. p. 81—82°/18 mm. (Found : C, 68·2; H, 6·4; Cl, 25·3. Calc. for C_8H_9Cl : C, 68·3; H, 6·4; Cl, 25·3%). The position of the chlorine atom in the molecule follows (*a*) from the ease with which it is eliminated by shaking with aqueous silver nitrate, (*b*) from the conversion of the compound into 2 : 3-diphenylbutane. 1-Phenylethyl chloride (7 g.) and sodium (2·5 g.) were left in dry ether (50 c.c.) for 5 days at 20°. The products isolated were : crystalline 2 : 3-diphenylbutane,

m. p. 123—124° (Found : C, 91·4 ; H, 8·6. Calc. for $C_{16}H_{18}$: C, 91·4 ; H, 8·6%), its liquid stereoisomer (Found : C, 91·8 ; H, 8·6%), and traces of unchanged halide and resin. These results are exactly as described by Ott (*Ber.*, 1928, **61**, 2142) for the action of sodium upon 1-phenylethyl chloride.

(2) Distyrene, b. p. 173—174°/16 mm., 135—137°/<1 mm. (Found : C, 92·1 ; H, 7·8 ; *M*, 207. Calc. for $C_{16}H_{16}$: C, 92·3 ; H, 7·7% ; *M*, 208). The distyrene generally contained a detectable trace of halogen, difficult to remove by distillation or by washing with water or silver nitrate solution. On oxidation with chromium trioxide in acetic acid, the distyrene gave benzoic acid, which is consistent with the structure (I). After recrystallisation from alcohol, the dibromide of the distyrene had m. p. 101—102·5° ; but this material was separated, by further recrystallisations from ether–petroleum ether mixture, into fractions having m. p. 129—130° (Found : Br, 43·1. Calc. for $C_{16}H_{16}Br_2$: Br, 43·4%) and 119—120° ; a very small amount of a further fraction, with m. p. 70—72°, was obtained from the mother-liquor. These results for the dibromide correspond closely to those found by Stoermer and Kootz (*loc. cit.*) for the dibromide of distyrene having the structure (I), the substance of m. p. 102° being a mixed crystal, separable into stereoisomers.

The extent of unsaturation of distyrene (cf. Tables II and III) was measured by running 5 c.c. of a carbon tetrachloride solution of distyrene into excess of standard iodine chloride (or bromine) solution in acetic acid, followed by titration of the residual halogenating agent (after varying times of exposure of the distyrene to the halogen, in order to ensure complete addition). Some specimen results are shown in Table V.

TABLE V.

Concn. $C_{16}H_{16}$, M	0·0609	0·0928	0·0923	0·0902
Concn. unsat. $C_{16}H_{16}$ found, M : after 5 mins.	0·0609	0·0886	0·0803	0·0253
after 10 mins.	0·0610	0·0887	0·0801	0·0251
% of unsat. isomer in $C_{16}H_{16}$	100	95·6	87·0	27·9

(3) Tristyrene, a faintly yellow, viscous oil, showing a pale-blue fluorescence, b. p. 214—215°/<1 mm. (Found for different preparations : C, 91·9, 92·1, 92·0, 91·7 ; H, 7·9, 7·6, 8·0, 8·0 ; *M*, 324, 312, 308, 311. Calc. for $C_{24}H_{24}$: C, 92·3 ; H, 7·7% ; *M*, 312). Attempts to prepare a dibromide gave only a semi-solid mass, which is not surprising in view of the number of possible stereoisomers.

(4) Tetrastyrene, a very viscous oil. A sample prepared from 4M-styrene and 0·04M-stannic chloride had b. p. 255—258°/<1 mm. (Found : C, 92·2 ; H, 7·8 ; *M*, 412. Calc. for $C_{32}H_{32}$: C, 92·3 ; H, 7·7% ; *M*, 416).

(5) Pentastyrene, b. p. 280—300°/<1 mm., *M*, 513 (calc. : 520), was isolated by distillation of the combined polymers from several reaction mixtures. It was exceedingly viscous.

Ozonisation Experiments.—The tri- and tetra-styrenes were ozonised in acetic acid solution. After decomposition of the ozonides with zinc and water, the resulting aldehydes were converted into their 2 : 4-dinitrophenylhydrazones. Benzaldehyde proved to be a principal product from both ozonisations, as would be expected from the structures (III) and (IV). The benzaldehyde 2 : 4-dinitrophenylhydrazone, separated by chromatography on a column of alumina, had the following characteristics : (*a*) from tristyrene (Found : C, 54·8 ; H, 3·8. Calc. for $C_{13}H_{10}O_4N_4$: C, 54·5 ; H, 3·5%), m. p. 236—237° ; mixed m. p. with authentic specimen, 233—234° ; (*b*) from tetrastyrene (Found : C, 54·6 ; H, 3·8%), m. p. 234—235° ; mixed m. p. with authentic specimen, 233·5—234·5° ; m. p. of authentic specimen, 234—235°.

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