CCXXX.—*Effects induced by the Phenyl Group. Part I. The Addition of Polar Reagents to Styrene and the Behaviour of the Halogenated Ethylbenzenes.*

By Frank Ashworth and George Norman Burkhardt.

One of the most striking exceptions to the Markownikoff rule was described by Posner in his work on the addition of phenyl mercaptan to double bonds (*Ber.*, 1905, **38**, 646). He allowed various unsymmetrical unsaturated compounds to remain in contact with phenyl mercaptan and oxidised the sulphides produced to sulphones. These he compared with the sulphones obtained by the action of sodium benzenesulphinate on the bromide which was formed by the addition of hydrogen bromide to the respective unsaturated hydrocarbons. In each case the products from the two methods were different. He assumed each to be a pure substance and deduced that phenyl mercaptan added in the opposite sense to hydrogen bromide; *e.g.*,

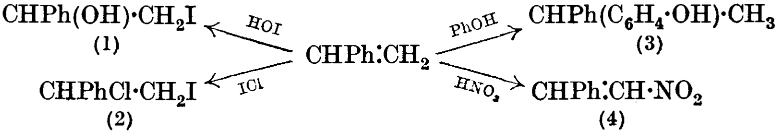
$$\begin{tikzcd}
& CHPhBr\cdot CH_3 \arrow[r, "Ph\cdot SO_2Na"] & \underset{\text{(I.)}}{CHPh(CH_3)\cdot SO_2Ph} \\
CHPh{:}CH_2 \arrow[ur, "HBr"] \arrow[dr, "Ph\cdot SH"'] & & \\
& \underset{\text{(II.)}}{CH_2Ph\cdot CH_2\cdot SPh} \arrow[r, "KMnO_4"] & \underset{\text{(III.)}}{CH_2Ph\cdot CH_2\cdot SO_2Ph}
\end{tikzcd}$$

He does not record tests to establish whether any of the products were mixtures, and assumes that the Markownikoff rule holds perfectly for the addition of hydrogen bromide. It is not clear, in the cases of trimethylethylene and camphene, that his initial material was pure and he notes that the same product was obtained in good yield from crude amylene as from trimethylethylene. The present investigation was primarily designed to test his conclusions in the case of styrene, where the pure hydrocarbon was readily available, but it was also necessary to examine the evidence on the effects induced in the side chain by the phenyl group, and particularly the mode of addition of hydrogen bromide and other polar reagents to styrene.

The addition of hydrogen bromide to styrene gave, as stated by Schramm (*Ber.*, 1893, **26**, 1710), only α-bromoethylbenzene. The product was compared with the bromides obtained from phenylmethylcarbinol and phenylethyl alcohol.

The addition of sodium bisulphite to styrene had previously been effected at 100° by Miller (*Annalen*, 1877, **189**, 340), but he did not identify the product. The reaction of ammonium bisulphite in cold dilute aqueous solution with styrene emulsified in it with kieselguhr (Kolker and Lapworth, J., 1925, **127**, 307) gave in 10 days a 10% yield of pure ethylbenzene-α-sulphonate, identified by comparison with the synthetic sulphonates obtained by the action of boiling ammonium sulphite on the α- and β-bromoethylbenzenes.

These additions are considered to take place by the combination of proton with the more anionoid carbon atom in the hydrocarbon (Kolker and Lapworth, *loc. cit.*; Lapworth, *Mem. Manchester Phil. Soc.*, 1925, **69**, xix; Robinson, J., 1926, 402). It must be assumed that the more anionoid centre in styrene is the ω-carbon atom in order to explain these additions and also such reactions as :

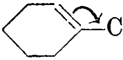


(1) Tiffeneau, *Compt. rend.*, 1907, **145**, 811; (2) Ingle, *J. Soc. Chem. Ind.*, 1902, **21**, 581; (3) Koenigs, *Ber.*, 1901, **34**, 3894; (4) Hofmann, *Annalen*, 1845, **53**, 297.

and a discussion of the origin of this selective anionoid activity shows what secondary effects are likely to be observed.

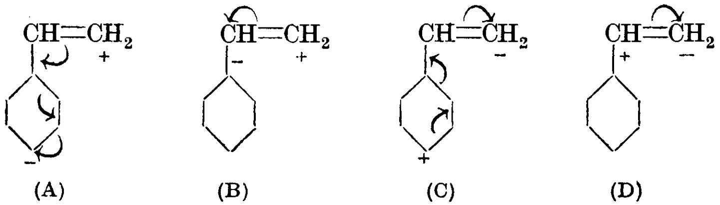
It is widely accepted that the general electrical effect of a group is to be estimated by a consideration of the dissociation constants of carboxylic acids, particularly those of acids in which conjugation can play little or no part (Flürscheim, J., 1909, **95**, 718; G. N. Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762; Allan, Oxford, Robinson, and Smith, J., 1926, 406). The constants of a suitable group of acids make it clear that, unlike saturated aliphatic or alicyclic groups, phenyl has a stronger attraction than hydrogen for electrons (negative general effect):

	$K \cdot 10^{-5}$.		$K \cdot 10^{-5}$.
Acetic	1·82	Benzoic	6·5
Propionic	1·31	Phenylacetic (?)	5·3
*cyclo*Hexanecarboxylic	1·32	Phenylpropionic	2·3

The general effect on the constant of benzoic acid will be greatly reduced by the conjugation  (IV), but may be somewhat increased by the steric effect of the phenyl group. The steric effect is, however, comparable in benzoic and *cyclo*hexanecarboxylic acids and both the steric and the conjugative effect are probably negligible in β-phenylpropionic acid, although here the general effect is also reduced by the length of the chain.

The chief result of this general effect on the side chain, apart from the conjugative effects which it may start, would be to make the β-electrons more available than those on the α-atom, but it is superimposed on any conjugative electronic displacements, in the manner discussed by Lapworth and Robinson (*Mem. Manchester Phil. Soc.*, 1928, **72**, 43) in their consideration of the *o* : *p* ratio in aromatic substitution.

Four types of conjugative electronic displacement affecting the reactions of the side chain are possible:



None of the known addition reactions (with the possible exception of that with phenyl mercaptan, which will be discussed later) requires phase (B) (the direction of polarisation which would be initiated by the general effect due to the phenyl group); which would be relatively inactive to kationoid reagents, as the anionoid activity of the α-carbon would be reduced by the holding in of the electrons on that atom by the attraction of the phenyl group (general effect) and also by the steric effect of the phenyl group. One would also anticipate that in this phase and in (D) the α-atom would reduce its charge by conjugation with the nucleus, although the work of Farmer and Thorpe on conjugated systems, of Scarborough, of Turner and of Kenyon and their collaborators on substituted diphenyl compounds, suggests that the transmission of such polarisations is not necessarily very complete.

The polarisation in (D) is directly opposed to the general effect and if it is initiated by an increase of covalency between the nuclear and the α-carbon atoms it approximates to phase (C). These are the phases which have the anionoid ω-carbon atom indicated by the reactions of the side chain, and something approximating to (C) must be considered the normal active phase of styrene.

This polarisation will not, however, explain the *o*-*p*-substitution in styrene and its derivatives, and the general effect of the vinyl group will tend to inhibit *o*-*p*-substitution, as this group has a greater attraction than hydrogen for electrons. This is clearly shown by the dissociation constants :

	$K . 10^{-5}$.		$K . 10^{-5}$.
Acetic acid	1·82	Vinylacetic acid	3·8
Butyric acid	1·47	Crotonic acid	2·2

(N.B. The general effect in crotonic acid is reduced by conjugation as in benzoic acid; compare above.)

Both the tendency to conjugate in the direction of (C) and (D) and the attraction of the side chain for electrons will be increased in such derivatives of styrene as ω-nitrostyrene and cinnamic ester and yet even in these cases *o*-*p*-substitution predominates. It can only be assumed that in styrene and all these derivatives there is some tendency to polarise in the manner (A) and this will have an activating effect on the *o*-*p*-positions, whereas the opposite polarisation (C) and the general effect will reduce the activity of all the positions. Hence the polarisation of type (A) will facilitate ordinary substitution in the nucleus and those of type (C) will be more inert in the nucleus and substitution will be facilitated only in the ω-position. This is in keeping with the fact that styrene is nitrated in this position first.

It is anticipated that the detailed application of these theoretical considerations will be made clearer by experiments which are in progress with derivatives of styrene containing substituents both in the side chain and in the nucleus.

Another type of evidence on the effects induced by the phenyl group was obtained by the action of boiling aqueous-alcoholic caustic potash on the halogenated ethylbenzenes. Under these conditions α-bromoethylbenzene gave quantitatively phenylmethylcarbinol; β-bromoethylbenzene gave only styrene; and styrene dibromide gave pure α-bromostyrene. The last fact was proved by hydrolysing the product with formic acid, isolating the aceto phenone produced in 92% yield, and showing that ω-bromostyrene, which is inert towards formic acid, was absent from the residue. This is contrary to much previous work summarised by Nef (*Annalen*, 1899, **308**, 273) as follows :

"It is obvious that alcoholic potassium acetate, water at 190°, and alcoholic potash with styrene dibromide all give a mixture of α- and ω-bromostyrene, since the product has not a constant boiling point and gives phenylpropiolic acid on treatment with sodium and carbon dioxide. This can only be derived from ω-bromostyrene."

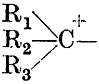
It was found, in the present investigation, that the boiling point rose rapidly from that of α-bromostyrene to that of unchanged styrene dibromide. The residue of the latter would account for the production of phenylpropiolic acid.

Neither α- nor β-bromoethylbenzene was reduced by hydriodic acid at 150° after four hours.

Ward has shown (J., 1927, 445) that the displacement of halogen in α-chloroethylbenzene is independent of the concentration of sodium hydroxide used and up to 50° gives phenylmethylcarbinol with optical inversion, but at 100° styrene, phenylmethylcarbinol, and αα′-diphenyldiethyl ether are formed. These facts he explains on the basis of a slow unimolecular reaction formulated in the way suggested by Nef :

$$C_6H_5{\cdot}CHCl{\cdot}CH_3 \longrightarrow C_6H_5{\cdot}\underset{/\ \backslash}{C}{\cdot}CH_3 + HCl$$

a step supposed to be followed by either (1) the addition of water, or (2) isomerisation to styrene, or (3) addition of phenylmethylcarbinol. He comments on the mechanism previously discussed by Phillips (J., 1925, **127**, 2567) dependent on the production of

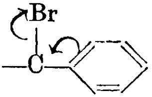


from a halogen compound by the removal of the halogen ion, but he retains the conception that, in such an ionisation, the hydrogen atom R_1 accompanies the halogen ion.

$$R_3{:}\underset{\underset{:\underset{\cdot\cdot}{Cl}:}{\cdot\cdot}}{\overset{\overset{R_2}{\cdot\cdot}}{C}}{:}H \longrightarrow R_3{:}\underset{\cdot}{\overset{\overset{R_2}{\cdot\cdot}}{C}}\cdot + H{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{:} \text{ not } R_3{:}\underset{\cdot\cdot}{\overset{\overset{R_2}{\cdot\cdot}}{C}}{:}H + {:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{:}$$

The inversion in the formation of phenylmethylcarbinol could be accounted for (compare Fischer, *Ber.*, 1907, **40**, 489 ; Lapworth and Mottram, *Mem. Manchester Phil. Soc.*, 1927, **71**, 63) if the removal of the halogen ion were dependent on one of the frequent approaches of the water or other solvent molecules, to the side of the α-carbon atom away from the halogen, occurring simultaneously with a rare polarisation of the molecule sufficient to ionise the halogen under these conditions. This mechanism would also account for other observations which Ward discusses, namely, that solutions of potassium cyanide, ammonia, and potassium acetate in ethyl alcohol all give α-phenyldiethyl ether as the main product.

Many investigators (compare Conant and Kerner, *J. Amer. Chem. Soc.*, 1924, **46**, 232) have observed that phenyl and carbonyl groups have similar effects on the halogen atoms in systems of the form $R\cdot[CH_2]_n\cdot Cl$ (R=phenyl, carbethoxyl, etc.), phenyl being less powerful than any carbonyl group, and the results of the present investigation also show such similarities. It is to be noted from a theoretical point of view, however, that while the general effect of phenyl and carboxyl is in the same direction relative to hydrogen, the conjugative effects will depend on the nature of the side chain and the various factors may operate in different ways in different reactions of halogen atoms in the side chain. The α-halogen in alkylbenzenes forms with the nucleus a type of allyloid system



(V) (Allan, Oxford, Robinson, and Smith, *loc. cit.*) in which the polarisation of the nucleus assists the tendency of the halogen atom to separate with a negative charge. This is in accord with the results of the investigations on the hydrolysis of substituted benzyl halides (*Ann. Reports*, 1927, **24**, 155), and also with the capacity of the phenyl group for stabilising a positively charged α-carbon atom which is clearly shown in the positive triphenylmethyl ion. The opposite polarisation (type A, p. 1793) and the general effect may account for its less powerful effect in stabilising a negative charge in the sodium derivative of triphenylmethyl.

In the case of the β-halogenated ethylbenzenes the effect of the phenyl group on the halogen atom, here separated from it by two single bonds, appears to be slight, judged by the low reactivity to potassium iodide in acetone (Conant and Kerner, *loc. cit.*). Assuming that the separation of the halogen ion is the first process in the production of styrene by the action of aqueous-alcoholic potassium hydroxide on ω-bromostyrene, this reaction will be dependent on the ease with which the electrons of the α-carbon atom co-ordinate with the ω-atom to form the double bond, as well as on the ease with which the halogen atom is removed. The conjugation with the nucleus (type C, p. 1793) will facilitate such co-ordination and the removal of the proton will follow. On the other hand, this reaction may be dependent on the tendency of the α-hydrogen to ionise, which will be increased by the opposite type of polarisation and the general effect.

The repetition of Posner's experiments gave the products which he obtained, and the sulphone from the addition of phenyl mercaptan to styrene was identical with that obtained by the action of sodium benzenesulphinate on β-bromoethylbenzene. The sulphide obtained from the addition was also shown to contain less than 2% of the α-isomeride, by comparing the boiling point and refractive index with those of the two synthetic sulphides. It is therefore clear that phenyl mercaptan adds to styrene in the opposite sense to hydrogen bromide and other polar reagents, and the theoretical considerations which satisfactorily correlate those normal additions will not serve in this case if the reaction takes place between the polarised ethylene bond and the hydrogen and thiophenoxide ions.

In a search for other evidence in favour of a special mechanism for this reaction the course of the addition of phenyl mercaptan to styrene was followed by observations of the very large contraction in volume which takes place during the reaction and also by determinations of the depression of the freezing point of benzene caused by mixtures of phenyl mercaptan and styrene. The rate of addition is greatly dependent on the intensity of illumination, and the increase in rate produced by exposure to sunlight continues for some time after the reaction vessel is returned to diffused light; but the reaction was not stopped in the dark and the product was always phenyl β-phenylethyl sulphide. A small percentage of piperidine had such a powerful retarding action on the addition that no change in volume was observed in diffused daylight even after several days, although a contraction took place in sunlight. The action of light is well known to produce or enhance abnormal polarisations and depolarisations in a wide range of reactions, and experiments are in progress with a view to obtaining evidence in favour of one or other of the possible alternative mechanisms for the interaction of mercaptans with ethylenic hydrocarbons.

A remarkable isomerisation was observed in an attempt to prepare phenyl-β-phenylethylsulphone (III) by reducing phenacylphenylsulphone (VI) with zinc amalgam and hydrochloric acid: a liquid sulphide was obtained which on oxidation with hot chromic acid was converted into phenyl-α-phenylethylsulphone (I). A similar migration of groups takes place when ω-bromoacetophenone is heated with yellow ammonium sulphide (Willgerodt, *Ber.*, 1889, **22**, 534).

$$\text{(VI.) } COPh{\cdot}CH_2{\cdot}SO_2Ph \longrightarrow \text{(II.) or } CHPh(CH_3){\cdot}SPh \text{ (VII.)} \longrightarrow \text{(I.)}$$

EXPERIMENTAL.

Preparation of the Monohalogen Derivatives of Ethylbenzene.—Phenylmethylcarbinol (b. p. 100°/15 mm.; 3 : 5-dinitrobenzoate

m. p. 95°), made by the action of magnesium phenyl bromide on acetaldehyde, was converted by gaseous hydrogen bromide into α-bromoethylbenzene. This, by the action of silver acetate suspended in ether, readily yielded phenylmethylcarbinyl acetate which on hydrolysis gave the carbinol free from any detectable proportion of β-phenylethyl alcohol, as was shown by the properties of its 3 : 5-dinitrobenzoate and the entire absence of the fragrance associated with the isomeric compound.

The β-chloroethylbenzene used in some of the experiments described later was made by converting glycol chlorohydrin into its *p*-toluenesulphonate and leaving this in contact with a cold ethereal solution of magnesium phenyl bromide for 36 hours; about an equal weight of a liquid, which was probably ethylene chlorobromide, was also produced (see Ferns and Lapworth, J., 1912, **101**, 273).

β-Bromoethylbenzene was made by heating β-phenylethyl alcohol with constant-boiling hydrobromic acid for 24 hours; it had b. p. 97°/12 mm., and was quite free from the pungent odour characteristic of the α-bromo-compound.

Action of Aqueous-alcoholic Potassium Hydroxide on the Isomeric Bromoethylbenzenes.—The two bromo-compounds, when heated on the water-bath under precisely similar conditions with aqueous-alcoholic potassium hydroxide (about 0·4*N*), lost all the halogen (as determined by the decrease in alkaline titres) within 30 minutes. In the product from the α-bromo-compound, no styrene whatever could be detected. The product from the β-bromo-compound was almost pure styrene and absorbed bromine (1 mol.), yielding styrene dibromide.

Addition Reactions of Styrene.—The styrene was made by Howard's method from cinnamic acid (J., 1861, **13**, 136).

(A.) *Addition of hydrogen bromide.* A mixture of styrene and a cold saturated solution of hydrogen bromide in glacial acetic acid was kept over-night and then poured into water, and the oil obtained was distilled (b. p. 95°/15 mm.). The product was nearly pure α-bromoethylbenzene, as it was converted, by means of silver acetate and alkali successively, into phenylmethylcarbinol which gave the characteristic 3 : 5-dinitrobenzoate (m. p. 95°) and had no detectable odour of the isomeric β-phenylethyl alcohol (3 : 5-dinitrobenzoate, m. p. 108°).

(B.) *Addition of ammonium hydrogen sulphite.* An emulsion of styrene (20 g.) with *N*/4-ammonium hydrogen sulphite (2 l.) and kieselguhr (100 g.) was kept with frequent shaking for 10 days. After filtration the liquid was boiled with excess of barium hydroxide until ammonia was expelled and worked up for soluble salts (compare J., 1925, **127**, 307); 8 g. (yield, about 16%) of colourless *barium α-phenylethanesulphonate* were obtained in bundles of small needles [Found: H_2O, 6·8; Ba (in anhydrous salt), 27·1. $(C_8H_9SO_3)_2Ba,2H_2O$ requires H_2O, 6·6%. $(C_8H_9SO_3)_2Ba$ requires Ba, 27·0%]. No alkyl sulphite could be detected (compare *loc. cit.*). A portion of the salt was converted into the amide, which separated from alcohol in feathery crystals, m. p. 121°.

The sulphonic derivatives were identical with those obtained from the ammonium salt produced when α-bromoethylbenzene was heated with aqueous ammonium sulphite for several hours (Found for the barium salt: H_2O, 6·9; Ba, in the anhydrous salt, 26·8%. Amide, feathery crystals, m. p. 121°, mixed m. p. 121°).

As α-bromoethylbenzene shows little or no tendency to become converted into styrene, the foregoing results indicate clearly that the sulphonic salt from styrene and hydrogen sulphite is the α-derivative of ethylbenzene. The conclusion, however, was checked by preparing the β-sulphonic acid.

β-Bromoethylbenzene (8 g.) was boiled with aqueous ammonium sulphite, and the solution worked up as usual with barium hydroxide. *Barium* β-*phenylethanesulphonate* (5 g.) was isolated in large, glistening plates [Found: H_2O, 3·4; Ba (in anhydrous salt), 26·8. $(C_8H_9SO_3)_2Ba,H_2O$ requires H_2O, 3·4%. $(C_8H_9SO_3)_2Ba$ requires Ba, 27·0%]. The sulphonamide melted at 124°.

(C.) *Addition of phenyl mercaptan.* The product obtained from styrene and phenyl mercaptan by Posner's method (*loc. cit.*) gave, on oxidation with cold dilute potassium permanganate solution and excess of sulphuric acid, the pure β-sulphone, m. p. 56—57°, identical with that prepared from β-bromoethylbenzene.

Phenyl α- and β-phenylethyl sulphides and the sulphide obtained by fractionating the addition product were unattacked by hot or cold neutral potassium permanganate, even when it contained manganese dioxide in suspension. The addition of bromine or of excess of dilute sulphuric acid caused rapid reduction of the permanganate. If the oxidation was carried out hot, a mixture of phenacylphenylsulphone (VI), m. p. 94—95°, and phenyl-β-phenylethylsulphone was obtained.

Phenyl-β-phenylethylsulphone (III) was prepared from β-bromoethylbenzene by boiling with an alcoholic solution of sodium benzenesulphinate for 12 hours and separated from carbon tetrachloride in feathery crystals, m. p. 56—57° (Found: S, 13·2. Calc. for $C_{14}H_{14}O_2S$: S, 13·0%). The sulphones could not be prepared from the chloroethylbenzenes, as the α-chloro-compound was converted into styrene and the β-isomeride was unchanged.

Pure phenyl α- and β-phenylethyl sulphides were prepared by heating sodium thiophenoxide (1·1 mols.) in alcoholic solution with α- or β-bromoethylbenzene (1·0 mol.), pouring the mixture into water, and extracting the product with carbon tetrachloride. The sulphides were distilled, heated for ½ hour under reduced pressure at 100° in a stream of carbon dioxide, and redistilled. The α-compound had b. p. 163—164°/15 mm. and n_D 1·6042; the β-compound, b. p. 188—189°/15 mm. and n_D 1·6082.

The whole product of the reaction between styrene and phenyl mercaptan was washed with alkali, dried, and fractionated. The distinction between unchanged styrene, sulphide, and a small residue (probably metastyrene) was clearly marked. The middle fraction (yield, 90%), b. p. 187—190°/15 mm., heated in a stream of carbon dioxide under reduced pressure at 100° and refractionated, gave the following refractive indices: first 6 drops, 1·6079; 9 c.c., 1·6082; 2 drops, 1·6085; residue, 1·6088. Fractions 1 and 2 after refractionation gave: first 2 drops, 1·6073; 10 drops, 1·6081; thirteenth drop and the remainder, 1·6082. This indicates less than 2% of α-isomeride in the product.

Experiments on the velocity of the reaction and photocatalysis. During the reaction of styrene and phenyl mercaptan a 10% contraction takes place, and the course of the reaction was followed by cooling a mixture of styrene (11 c.c.) and phenyl mercaptan (10 c.c.) in a glass tube (0·2 to 0·5 cm. bore) in running water, marking the level of the meniscus, sealing the tube, and marking the level from time to time. As the velocity is influenced by light, the two reagents were distilled in only the light of a Bunsen flame (the mercaptan was distilled in hydrogen to prevent the formation of disulphide), and two tubes were prepared as described above, marked and sealed in a similar light, and left in a dark room. The part of each tube containing the liquid was kept inside rubber tubing down which water was running and the subsequent marks were made with a minimum of light in the dark room. The two reactions proceeded at the same rate. After 17½ hours one tube was taken into sunlight, the water-cooling being continued. The contraction was nearly doubled in the next 15 minutes and was practically complete after 1 hour. The other tube in the dark showed no signs of reaching the same limit after 3 weeks.

Time (hrs.)	0·1	1·5	2·5	14·0	17·5	17·75	18·0	18·25
Contraction (cm.) in tube I in dark	0·5	0·75	1·05	2·15	2·35	4·0*	4·4*	4·7*
Contraction (cm.) in tube II in dark	0·6	0·8	1·1	2·15	2·3			
Time (days)	1·5	2·5	3·5	4·5	6·5	8·5	22·5	25·5
Contraction (cm.) in tube I in light	4·9	4·9				4·9		
Contraction (cm.) in tube II in dark	2·6	2·95	3·25	3·4	3·6	3·75	3·8	3·8

* In sunlight.

The phenyl mercaptan remaining in the reaction carried out in the dark was extracted in alkali and the sulphide which was distilled out of the residue was shown to contain no detectable amount of the α-isomeride by determinations of the refractive index and boiling point.

A side tube was inserted about 70 cm. from the lower end of the reaction tube, the mixture was introduced until it overflowed from the side tube, and a similar experiment was carried out entirely in the dark. The speed was similar to that in the previous experiments before taking into sunlight.

Cryoscopic evidence on the course of the reaction [with CECIL ROBINS]. The freezing points were taken of solutions of phenyl mercaptan and of styrene in suitable amounts of benzene, and also the freezing points of the mixed solutions, with a view to determining whether any considerable amount of association took place quickly, followed by a photocatalytic depolarisation. No such association was observed and the rate of combination appeared to be in agreement with the velocity measured by contraction. In this case, however, it was clear that the reaction did not slow down again at once when the tube was returned to diffused light.

Action of Alcoholic Potassium Hydroxide on Styrene Dibromide.—Styrene dibromide (Glaser, *Annalen*, 1870, **154**, 164) (26·4 g.) was boiled in alcoholic solution with potassium hydroxide (1 mol.), the alcohol removed by distillation, and the oily product distilled in a vacuum. No fraction was obtained between α-bromostyrene and styrene dibromide.

The product was almost instantly attacked by boiling formic acid, the odour of acetophenone becoming perceptible. As β-bromostyrene was found to be very stable towards boiling formic acid, undergoing but slight hydrolysis after 20 minutes, this observation, which finds a parallel in the ready hydrolysis of α-chlorostyrene by hydrochloric acid, suggested a means of detecting β-bromostyrene when mixed with the α-isomeride.

0·774 G. of the lower-boiling portion of the product from styrene dibromide was boiled for about 5 minutes with formic acid, and sodium acetate and semicarbazide hydrochloride were then added; acetophenonesemicarbazone (0·653 g.; 92% of the theoretical yield) was deposited. It is evident that at least 92% of the oil consisted of α-bromostyrene. No trace of β-bromostyrene (easily detected by its powerful hyacinth-like odour) could be found in the liquor after the acetophenone had been removed. As a small quantity of unchanged styrene dibromide was present, having escaped the fractionation process, it is clear that removal of hydrogen bromide from styrene dibromide takes place almost solely in one direction.

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