43. *Rubber, Polyisoprenes, and Allied Compounds. Part VI. The Mechanism of Halogen-substitution Reactions, and the Additive Halogenation of Rubber and of Dihydromyrcene.*

By George F. Bloomfield.

The chlorination of *cyclo*hexene by chlorine or by sulphuryl chloride (in the absence of a peroxide catalyst) yields substituted as well as additive chlorination product , and the former retain in full the original olefinic unsaturation as indicated by iodine-value determination; but whereas sulphuryl chloride forms only the additive dichloride and a monochloro-olefin which is substituted exclusively in the 3-position, yet chlorine yields a mixture of saturated trichloro-derivative (chloro-substituted addition product) and isomeric monochloro-olefins (3- and 4-substituted), together with some additive dichloride.

No evidence of substitution at the ethylenic methine carbon atom has been obtained in the chlorination of *cyclo*hexene, dihydromyrcene, and rubber by chlorine. The diminished unsaturation of the chloro-substitution products of the last two hydrocarbons is attributed to cyclisation—a process which is complete in the case of rubber, but affects only a minor proportion of the molecules of dihydromyrcene. The same cyclising tendency appears in the substitutive bromination of rubber by *N*-bromosuccinimide, but not to any appreciable extent in the similar bromination of dihydromyrcene.

Additive chlorination products are formed when rubber is brought into reaction with chlorine liberated by the thermal dissociation of phenyliododichloride, or of sulphuryl chloride in the presence of a peroxide. The mode of reaction of bromine with rubber, about which many contradictory statements have been made, is found to be entirely additive if the solvent contains a trace of alcohol and the temperature is 0°. A method based on bromine addition may be used for estimating rubber hydrocarbon. Additive bromo- and chloro-derivatives of rubber are comparatively stable and give no indication of the spontaneous elimination of halogen acid either through cyclisation reactions or the re-formation of double bonds at temperatures up to 80°.

The provision of chlorine in free-radical form appears to be an essential condition for obtaining the wholly additive chlorination of rubber and allied olefins. The reaction of molecular chlorine or bromine, on the other hand, follows a course which can be adequately explained by the initial formation of an activated dihalide, the fate of which is determined by the nature of the olefinic system and the experimental conditions.

The chlorination of rubber presents a peculiar feature in that the observed unsaturation of the substitutive chlorination products is considerably lower than would be anticipated for a purely substitutive mode of reaction by the halogen (cf. Part IV, J., 1943, 289). The possible exercise by the substituent chlorine atoms present in the groups $-CHCl\cdot C{:}C-$ or $-CH_2\cdot CCl{:}C-$ of an inhibiting influence on the additive capacity of the double bond can be investigated by examination of halogenated derivatives of rubber and of allied olefins in which the position of the substituent halogen can be established. The work of Ziegler *et al.* (*Annalen*, 1942, **551**, 80) has not only drawn attention to an admirable reagent (*N*-bromosuccinimide) for the halogenation of olefins in the 3-position, but has also provided a method for estimating 3-substituted bromine by interaction with alcoholic silver nitrate.

The Action of Chlorine on cyclo*Hexene.*—The chlorination of *cyclo*hexene appeared to be particularly well suited for examining the details of the chlorination process as it occurs in simple olefins. The behaviour of *cyclo*hexene towards chlorine, however, differed from that of the olefins studied in Part IV in that, although the overall chlorination reaction was mainly substitutive (59%, thus giving monochloro*cyclo*hexene together with trichloro*cyclo*hexane in which both substitution and addition of chlorine had occurred), yet the major product was the additive dichloride, dichloro*cyclo*hexane. The monochloro*cyclo*hexene had the correct iodine value when allowance was made for the presence of a small proportion of dichloro*cyclo*hexane from which the chloro-olefin not could be completely freed.

Although peroxide-catalysed chlorination by sulphuryl chloride is normally additive in habit (Kharasch and Brown, *J. Amer. Chem. Soc.*, 1939, **61**, 3432), it was found that *cyclo*hexene could none the less be chlorinated in a partly substitutive manner by this reagent if brought to reaction in the presence of an antioxidant or a halogen carrier. The resulting chloro*cyclo*hexene again had the correct iodine value, but whereas all of the chlorine in this chloro-olefin could be removed by a brief treatment with alcoholic silver nitrate, only 80—85% of the chlorine was similarly removed from the chloro*cyclo*hexene resulting from the action of chlorine on *cyclo*hexene (see table).* Now, since only an insignificant proportion of the chlorine in 1-chloro*cyclo*hexene, and only a relatively small proportion of that in monochloro*cyclo*hexane were removable by comparable treatment with silver nitrate, and, further, since 1-chloro*cyclo*hexene was found to add iodine chloride very incompletely, doubtless owing to the inhibiting effect of the 1-substituted chlorine (cf. dichloroethylene), it must be concluded that the chloro*cyclo*hexene resulting from chlorination by sulphuryl chloride is wholly 3-chloro*cyclo*hexene, whereas that resulting from the chlorination by chlorine is a mixture of this (*ca.* 80%) with a smaller proportion (*ca.* 20%) of an isomer, likely to be 4-chloro*cyclo*hexene, but containing no 1-chloro*cyclo*hexene. (The 4-chloro*cyclo*hexene is present in slightly greater proportion in the more volatile fractions of the mixture of isomers.)

Unsaturation of Halogen-substituted Polyisoprenes.—On the assumption that the above considerations apply to the chlorination of dihydromyrcene and of rubber, it must be considered highly improbable that the diminished iodine value observed for mono- and di-chloro-substituted dihydromyrcene and for monochloro-substituted rubber can be attributed to an inhibiting effect of the substituent chlorine atom, and hence cyclisation must be

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* Additive dichlorides were comparatively stable to the silver nitrate reagent.

accepted as the most probable alternative cause. This view finds support in the behaviour of the afore-mentioned substituted derivatives of dihydromyrcene and of rubber towards silver nitrate (see table).

Reaction of Some Halogenated Substances with Alcoholic Silver Nitrate.

Substance.	Method of preparation.	$100 \times \frac{\text{Reactive halogen}}{\text{Total halogen}}$
Chloro*cyclo*hexene, C_6H_9Cl	Cl_2 + *cyclo*hexene	80—85
,, ,,	SO_2Cl_2 + *cyclo*hexene + antioxidant	100
1-Chloro*cyclo*hexene, C_6H_9Cl	PCl_5 + *cyclo*hexanone	3
Chloro*cyclo*hexane, $C_6H_{11}Cl$		8
Bromo*cyclo*hexane, $C_6H_{11}Br$		99
Dichloro*cyclo*hexane, $C_6H_{10}Cl_2$	SO_2Cl_2 + *cyclo*hexene + peroxide	1
Chlorodihydromyrcene, $C_{10}H_{17}Cl$	Cl_2 + dihydromyrcene	85—90
Bromodihydromyrcene, $C_{10}H_{17}Br$	*N*-Bromosuccinimide + dihydromyrcene	99
Dihydromyrcene dichloride, $C_{10}H_{18}Cl_2$	SO_2Cl_2 + dihydromyrcene + peroxide	15
Chlororubber, $C_{10}H_{15}Cl$	Cl_2 + rubber	88
,, C_5H_7Cl	,, ,,	70
,, $C_{10}H_{15}Cl$	SO_2Cl_2 + rubber + antioxidant	90
Bromorubber, $C_{10}H_{15}Br$	*N*-Bromosuccinimide + rubber	94
Rubber dichloride, $C_5H_8Cl_2$	SO_2Cl_2 + rubber + peroxide	6

If the small proportion of the chlorine in these derivatives which is unreactive to silver nitrate is attributed to 1-substituted products, then the amount of these is quite insufficient to account for the whole of the observed lowering of iodine value; indeed, it seems more justifiable, as in the case of *cyclo*hexene, to attribute the unreactive part of the chlorine to substitution in positions other than the methinic and α-methylenic carbon atoms (*i.e.*, to substitution in the β- or β′-positions) and such substitution would cause no lowering of the iodine value. Furthermore, monobromodihydromyrcene obtained by the action of *N*-bromosuccinimide on dihydromyrcene has almost the theoretical iodine value (cf. low iodine value of monochlorodihydromyrcene obtained by the action of chlorine on dihydromyrcene), and all of its halogen is removed by silver nitrate.* The behaviour of the bromo-rubber similarly obtained is not, however, so satisfactory, its iodine value being considerably lower than that required for simple bromine-substitution. Since there is no justification for assuming that the mode of reaction of *N*-bromosuccinimide should be any different in the case of rubber from that established with the considerable number of olefins which have been successfully brominated at the α-methylenic position, this reduction of unsaturation is again attributed to cyclisation.

The further chlorination of monochloro-substituted rubber provides evidence in support of a cyclised structure. Reference has already been made in Part IV to the additive uptake of only 0·5 mol. of chlorine per C_5H_7Cl unit, which is in accordance with the observed unsaturation. It is now found that an excess of sulphuryl chloride reacting under additive conditions in the presence of a peroxidic catalyst also brings about the addition of only 0·5 mol. of halogen, the rest reacting substitutively. It is therefore concluded that the chlorination of polyisoprenes is particularly prone to proceed by a cyclisation mechanism. The cyclisation appears to be complete with rubber (leaving $|_1^{=}$ per two C_5H_7Cl units) but only partial with dihydromyrcene (*ca.* 30% of molecules cyclised); no separation of cyclised and uncyclised portions is practicable owing to the proximity of boiling points.

Formation of Polychloro-derivatives in Chlorination Reactions.—Although the ratio of liberated hydrogen chloride to reacted chlorine permits of the formation of only a monosubstituted chloro-derivative from rubber, the possibility of tri- or poly-chloride formation as well as additive chlorination must be taken into account when this ratio falls below unity. In the case of *cyclo*hexene the formation of a considerable proportion of trichloro*cyclo*hexane has been established, the relative proportions of the chlorination products from this olefin being dichloro*cyclo*hexane 47%, trichloro*cyclo*hexane 23%, 3-chloro*cyclo*hexene 19%, 4-chloro*cyclo*hexene 5%, residue (containing much chlorine) 6%. 1-Methyl*cyclo*hexene appears to yield mainly monochloromethyl*cyclo*hexene and trichloromethyl*cyclo*hexane with relatively little dichloromethyl*cyclo*hexane. Where these polychloro-derivatives are formed the yield of monochloro-olefin is considerably less than would be expected from the proportion of hydrogen chloride formed, *e.g.*, the simultaneous progress of reactions (1) and (2)

$$\mathrm{RH}|_1^{=} + \mathrm{Cl_2} \longrightarrow \mathrm{RCl}|_1^{=} + \mathrm{HCl} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{RH}|_1^{=} + 2\mathrm{Cl_2} \longrightarrow \mathrm{RCl_3} + \mathrm{HCl} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

satisfies an overall reaction which is apparently 67% substitutive as measured by the hydrogen chloride : chlorine ratio, but the yield of monochloro-substitution product is only 33% when calculated on the amount of chlorine reacting.

Polychloride formation is greatest with *cyclo*hexene, even when the hydrocarbon is present in considerable excess; doubtless, the increase in monosubstitutive reaction in 1-methyl*cyclo*hexene, dihydromyrcene, squalene, and rubber is to be attributed to the influence of the 1-methyl substituent. No chloro-derivatives other than monochloro-olefin and additive dichloride are, however, obtained when sulphuryl chloride is used as a sub-

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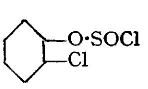
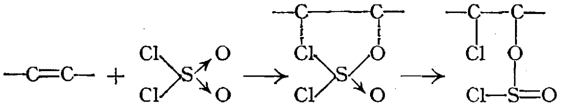
* The lability of substituted *bromine* towards alcoholic silver nitrate is, however, no certain criterion of the absence of substitution in the β-position, for, in contrast to the anticipated behaviour of the halogen in 4-chloro*cyclo*hexene, bromine located in the β-(or 4-) position may quite well be labile since the halogen in bromo*cyclo*hexane, unlike that in chloro*cyclo*hexane, is wholly reactive towards alcoholic silver nitrate.

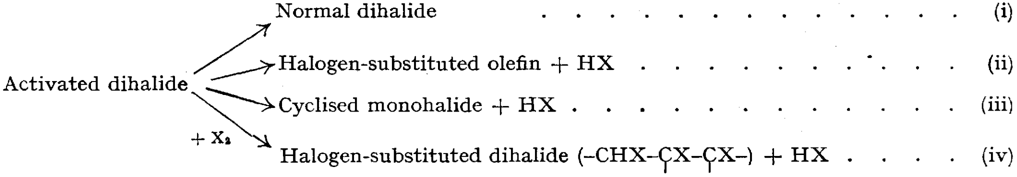
stitutive chlorinating agent, although in the absence of a halogen carrier a small amount of the chloride of 2-*chloro*cyclo*hexyl sulphite* (inset) is formed (cf. chlorides of alkyl sulphites, Stähler and Schirm, *Ber.*, 1911, **44**, 319). This substance is assumed to have resulted by addition of sulphuryl chloride to the ethylenic linkage since Kharasch *et al.* (*J. Amer. Chem. Soc.*, 1939, **61**, 3089; 1940, **62**, 925, 2393) have shown that substitution of –SO_2Cl groups by a free-radical chain mechanism leads to the formation of sulphonyl chlorides. Since the sulphur atom is linked to the carbon atom through oxygen the additive reaction is thought to pursue the molecular course :





The intermediate formation of the chloride of 2-chloro*cyclo*hexyl sulphite has been assumed by Friese and Djiang (*Ber.*, 1938, **71**, 667) to occur in the reaction of sulphuryl chloride with *cyclo*hexene and acetic acid, whereby 1-chloro-2-acetoxy*cyclo*hexene is isolated as a final product.

The reaction of chlorine with rubber and with allied olefins, which does not appear to follow a free-radical course since it proceeds with equal facility in darkness and in light and in the presence or absence of oxygen, antioxidants, or peroxides, is very probably dependent upon the activating effect of the –CMe:C– system on the left-hand α-methylene hydrogen atoms of –CH_2·CMe:CH·CH_2– (Farmer and Sundralingam, J., 1942, 121) leading to preferential substitution at this position, and this view is supported by the decrease in additive reaction in passing from *cyclo*hexene to 1-methyl*cyclo*hexene, dihydromyrcene, squalene, and rubber, although the mode of reaction with rubber may be influenced by the readiness with which this undergoes cyclisation. It is, however, necessary to consider whether the reaction of molecular chlorine is truly substitutive or whether it involves double bond re-formation or cyclisation changes, either spontaneous or promoted by an intermediate additive chloride of high energy content. The very considerable stability of the additive chlorides of *cyclo*hexene, dihydromyrcene, and rubber (see below) renders extremely doubtful any hypothesis of secondary decomposition of an additive dichloride. The possibility of an induced decomposition of an additive dichloride (cf. decomposition of ethyl chloride in the presence of chlorine, Rust and Vaughan, *J. Org. Chem.*, 1940, **5**, 449) has been examined by submitting an additive dichloride of rubber to the action of chlorine; although some substitutive reaction occurred whereby the chlorine content was raised, there was no evidence of any significant elimination of hydrogen chloride other than that accounted for by the substitutively-reacting chlorine, nor was there evidence of any double bond re-formation. There still remains the possibility that reaction proceeds by a chain mechanism involving a resonance hybrid (Anantakrishnan and Venkataraman, *Chem. Reviews*, 1943, **33**, 27) or alternatively by formation of an activated additive dihalide of high energy content (Stewart *et al.*, *J. Amer. Chem. Soc.*, 1929, **51**, 3082 *et seq.*), deactivation of the latter proceeding in one or more of the following ways according to the prevailing reaction conditions, the energy associated with the activated dihalide, and the nature of the olefinic system :



Normal dihalide . . . . (i)
Halogen-substituted olefin + HX . . . . (ii)
Cyclised monohalide + HX . . . . (iii)
Halogen-substituted dihalide (–CHX–CX–CX–) + HX . . . . (iv)

Whether the halogenation reactions now under consideration are actually substitutive, or whether they proceed in accordance with the above hypotheses, cannot be finally established from the evidence available, but the bulk of the evidence rather favours a mechanism conforming with Stewart's proposals. The cyclisation mechanism (iii) seems somewhat preferable to that suggested in Part IV (scheme ii), since in the new scheme it is no longer necessary to assume a different point of attack of the halogen in the polyisoprene and *cyclo*hexene systems.

The Additive Halogenation of Rubber and of Dihydromyrcene.—It seemed desirable to examine some halogenation reactions in which the halogen is generated by decomposition of an easily dissociated halogeno-reagent. Phenyliododichloride is a suitable reagent for this purpose and has been shown by Garvey, Halley, and Allen (*J. Amer. Chem. Soc.*, 1937, **59**, 1827) to form additive chlorination products with *cyclo*hexene and other olefins. These workers have also shown that phenyliododifluoride reacts with rubber to give hydrogen fluoride and a monofluoro-rubber, the latter being formed either substitutively or by decomposition of an unstable difluoride. It was accordingly anticipated that phenyliododichloride would yield a monochloro-rubber and hydrogen chloride in the same way as chlorine itself, and indeed, Garvey *et al.* have stated generally that the mode of chlorination by this reagent is the same as that of chlorine. Surprisingly, this reagent has been found to halogenate rubber in an almost exclusively *additive* way, yielding a dichloride $(C_5H_8Cl_2)_n$ of considerable thermal stability compared with products of substitutive chlorination.

The chlorinating action of peroxide-catalysed sulphuryl chloride (cf. Kharasch and Brown, *J. Amer. Chem. Soc.*, 1939, **61**, 2142) has already been used for the addition of chlorine at the ethylenic linkage of *cyclo*hexene (*idem, ibid.*, p. 3432), and this reagent has now enabled chlorine addition products to be obtained from dihydromyrcene and from rubber, although some difficulty was experienced in obtaining wholly additive reaction with specimens of rubber which had not been submitted to careful purification to remove naturally occurring antioxidants.

The formation of a stable additive dichloride of rubber is of considerable theoretical interest, since a purely additive reaction free from substitution has not hitherto been achieved. An additive dibromide $(C_5H_8Br_2)_n$, on the other hand, was long ago prepared (Gladstone and Hibbert, J., 1888, **53**, 682; Weber, *Ber.*, 1900, **33**, 786), and indeed, attempts have been made to estimate rubber hydrocarbon by bromine addition, although the formation of the dibromide has not generally been accomplished without the liberation of some proportion of hydrogen bromide, and the dibromide when isolated has been reported to liberate hydrogen bromide vigorously at 50—60° (Weber, *loc. cit.*). Substitutive side reaction has, however, been minimised by operating at 0° in chloroform (Hinrichsen and Kindscher, *Z. anorg. Chem.*, 1913, **81**, 70).

A more detailed study of the manner of reaction of bromine with rubber appeared desirable, since it seemed to occupy an interesting intermediate position between the exclusively substitutive mode of reaction of chlorine and the exclusively additive mode of reaction of iodine chloride (Kemp, *Ind. Eng. Chem. Anal.*, 1934, **6**, 52). When rubber was acted upon by bromine at temperatures between 0° and − 40° no difficulty was experienced in obtaining exclusively additive reaction provided that some chloroform was present, and the bromide so obtained underwent no decomposition at all on heating to 80°, nor was there any evidence of change in unsaturation, such as might arise from double bond re-formation or from cyclisation, as a result of mild heat treatment of a partly brominated product. The effect of chloroform in suppressing substitutive reaction is probably due to traces of alcohol normally present in this solvent rather than to any special characteristic of the solvent itself, since addition of alcohol enabled bromination to be conducted in carbon tetrachloride without hydrogen bromide formation: in this connection it is of interest that an alcoholic medium has been found helpful in suppressing substitutive reaction in the preparation of dihydromyrcene tetrabromide (Schimmel's Report, Oct. 1911, 128).

In spite of statements to the contrary in the literature, bromine addition has in the present work been found satisfactory for estimating rubber hydrocarbon and has the special merit of speedy operation.

Mechanism of Additive Halogenation Reactions.—Kharasch and Brown (*J. Amer. Chem. Soc.*, 1940, **62**, 925) suggest that the twofold mode of reaction of sulphuryl chloride can be explained by the following hypotheses: (1) The peroxide-catalysed reaction furnishes a source of chlorine *atoms* and chlorination proceeds by a free-radical chain mechanism. (2) Thermal dissociation of the reagent provides some other form of active chlorine which reacts in the same way as chlorine itself. In the former case the reaction mechanism is of the same nature as that proposed for photochemical chlorination (Schumacher and Stauff, *Angew. Chem.*, 1936, **49**, 613; 1940, **53**, 501; *Z. Elektrochem.*, 1942, **48**, 271, 550), which even in a simple substitutive reaction may follow a course quite different from that promoted by chlorine in the absence of direct illumination, for whereas photochemical chlorination with chlorine (Michael and Garner, *Ber.*, 1901, **34**, 4046) and the peroxide-catalysed reaction of sulphuryl chloride both lead to substitution of fatty acids in the β-position (mainly), yet non-photochemical chlorination carried out with chlorine (Markownikow, *Annalen*, 1870, **153**, 241; Wolffenstein and Rolle, *Ber.*, 1908, **41**, 733) or with sulphuryl chloride in the presence of a halogen carrier yields α-substituted acids.

If these hypotheses are accepted in the present investigation, then, if it can be shown that chlorination by phenyliododichloride follows a free-radical course, there will be reason to think that the presentation of the chlorine in free radical (*i.e.*, atomic) form is also an essential condition for the additive chlorination of rubber and of allied olefins. Although the reaction with phenyliododichloride gave in practice no obvious sign of being peroxide-catalysed, there was evidence of an underlying free-radical chain mechanism in the fact that the reaction in the presence of quinol was very slow and incomplete and was also to a considerable extent substitutive in character. Zappi and Degiorgi (*Bull. Soc. chim.*, 1931, **49**, 1035; 1932, **51**, 1605) have differentiated between the electrical charges associated with the two chlorine atoms in phenyliododichloride, hence the separation of a free chlorine atom by thermal dissociation (equation 1) is not an unlikely initiating step, although in the presence of a peroxide the steps shown in equations 2—4 represent a more probable course of reaction. After

$$\mathrm{PhICl_2} \longrightarrow \mathrm{PhICl^{\bullet}} + \mathrm{Cl^{\bullet}} \qquad (1)$$

$$\mathrm{Peroxide} \longrightarrow \mathrm{R^{\bullet}} \qquad (2)$$

$$\mathrm{R^{\bullet}} + \mathrm{PhICl_2} \longrightarrow \mathrm{RCl} + \mathrm{PhICl^{\bullet}} \qquad (3)$$

$$\mathrm{PhICl^{\bullet}} \longrightarrow \mathrm{PhI} + \mathrm{Cl^{\bullet}} \qquad (4)$$

the liberation of atomic chlorine the reaction could quite well proceed by the chain mechanism proposed for sulphuryl chloride (Kharasch and Brown, *loc. cit.*).

Attempts have been made to confirm the requirement of atomic chlorine for obtaining the additive chlorination of rubber by bringing chlorine into contact with a rubber solution which was irradiated by a powerful ultra-violet lamp, and also with a rubber solution containing benzoyl peroxide (the latter experiment being conducted at 80°), but in neither case was there any obvious departure from the usual exclusively substitutive reaction of the chlorine. Probably the substitutive reaction of molecular chlorine proceeds more readily than the additive reaction of free radical chlorine when both forms of the reagent are present.

An explanation of the substitutive bromination of olefins by *N*-bromosuccinimide presents rather more difficulty, but a chain mechanism of the type represented by equations 5—8 provides a satisfactory explanation if it be assumed that the major influence directing the reaction is the tendency of the  $\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2{-}CO}\end{matrix}\!\!>\!\mathrm{N^{\bullet}}$ radical (formed in the first instance by thermal dissociation of the bromo-compound) to accept hydrogen (6) and that the α-methylene hydrogen atom is the one most readily detached from the $-CH_2{\cdot}CR{:}CH-$ system.

$$(C_4H_4O_2)N{\cdot}Br \longrightarrow (C_4H_4O_2)N^{\bullet} + Br^{\bullet} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$-CH_2{\cdot}C{:}C- + (C_4H_4O_2)N^{\bullet} \longrightarrow -\dot{C}H{\cdot}C{:}C- + (C_4H_4O_2)NH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

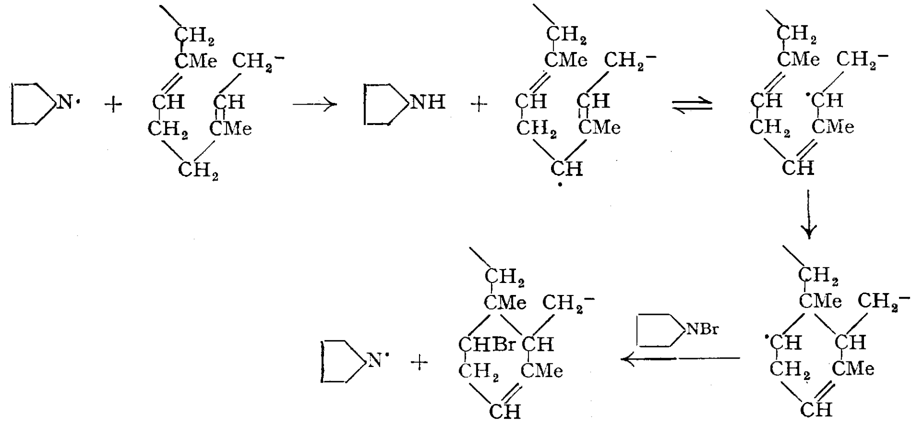
$$-\dot{C}H{\cdot}C{:}C- + Br^{\bullet} \longrightarrow -CHBr{\cdot}C{:}C- \text{ (or } -C{:}C{\cdot}CHBr-) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

(chain termination)

$$-\dot{C}H{\cdot}C{:}C- + (C_4H_4O_2)N{\cdot}Br \longrightarrow \begin{matrix} -CHBr{\cdot}C{:}C- \\ \text{(or } -C{:}C{\cdot}CHBr-) \end{matrix} + (C_4H_4O_2)N^{\bullet} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

(chain propagation)

The production of isomeric bromo-substituted products in reactions (7) and (8) (cf. Ziegler *et al.*, *loc. cit.*) is to be anticipated as a result of resonance in the $-\dot{C}H{\cdot}C{:}C-$ radical (Farmer, Koch, and Sutton, J., 1943, 541), and the very considerable degree of cyclisation promoted by the action of *N*-bromosuccinimide on rubber can be similarly explained by the following mechanism.



EXPERIMENTAL.

(Microanalyses were carried out by Dr. W. T. Chambers and Miss H. Rhodes.)

In general, the chlorination apparatus described in Part IV (Fig. 1) was used. For halogenating agents other than chlorine the graduated tube *A* was removed; liquid reagents were introduced beneath the surface of the rubber solution in *B*, and for this purpose a dropping funnel was fitted. A stirrer was also introduced into *B* to ensure thorough mixing of liquid and solid reagents. Gaseous reaction products were swept into an absorption system by means of a brisk stream of purified nitrogen which also prevented access of air to the reaction system.

Treatment of Halogenated Products with Alcoholic Silver Nitrate.—The sample (0·1 g.) was dissolved in a little alcohol, alcoholic silver nitrate (25 c.c., 0·1N) added, and the solution heated under reflux for 30 mins. After cooling, the solution was suitably diluted and an aliquot portion was added to an excess of sodium chloride solution (0·025N), the excess being estimated volumetrically with silver nitrate solution (0·025N), dichlorofluorescein being used as internal indicator.

Alcohol-insoluble substances (*e.g.*, halogenated rubbers) were dissolved in benzene (0·1 g. in 100 c.c.), and to the solution, warmed to 50—60°, was added a mixture (50 c.c.) of equal volumes of alcoholic silver nitrate (0·1N) and benzene. After refluxing for 1 hour and subsequently cooling, the solution was washed with successive small quantities of water until free from silver; the washings were combined, and an aliquot portion treated as above.

The proportion of the halogen which reacted with the silver nitrate, expressed as a % of the halogen in the sample, is hereinafter described as "reactive halogen."

Halogenation with Chlorine.

The Action of Chlorine on cyclo*Hexene.*—Peroxide-free *cyclo*hexene (20 c.c.; prepared by shaking with aqueous sodium hyposulphite, drying in an inert atmosphere, and distilling in a stream of purified nitrogen) was treated with chlorine (14·4 g.) at 80° in the absence of oxygen and in very subdued light: 4·33 g. of hydrogen chloride were formed, corresponding to 59% substitutive reaction. Distillation of the liquid product (26·2 g.) gave the following fractions: (i) unreacted *cyclo*hexene; (ii) b. p. < 40°/13 mm. (1·0 g.); (iii) b. p. 40—50°/13 mm. (2·0 g.); (iv) b. p. 50—60°/13 mm. (2·5 g.); (v) b. p. 60—68°/13 mm. (Found: *I.V.*, 31) (2·4 g.); (vi) b. p. 68—70°/13 mm. (Found: *I.V.*, 9) (1·6 g.); (vii) b. p. 70—72°/13 mm. (2·1 g.); (viii) b. p. 30—52°/0·01 mm. (2·1 g.); (ix) b. p. 52—53°/0·01 mm. (2·8 g.); (x) b. p. 53—60°/0·01 mm. (0·4 g.); (xi) small residue (1·0 g.). Fractions (viii)—(x) were saturated to iodine chloride and to bromine, (vi) and (vii) were mainly 1 : 2-dichloro*cyclo*hexane (cf. product of reaction of sulphuryl chloride with *cyclo*hexene, p. 119), and (ix) was a trichloro*cyclo*hexane (Found: Cl, 56·7. Calc. for $C_6H_9Cl_3$: Cl, 56·8%). The bulk of the unsaturated products were in the more volatile fractions; (iii) and (iv) were accordingly united and redistilled, yielding fractions (xii) b. p. 38—40°/13 mm. (1·2 g.); (xiii) b. p. 40—43°/13 mm. (1·5 g.); (xiv) b. p. 43—65°/13 mm. (0·6 g.); and (xv) b. p. 65—68°/13 mm. (1·2 g.). The last fraction was saturated to iodine chloride and was added to the dichloro*cyclo*hexane fractions. The foregoing separative procedure thus yielded the following main products: monochloro*cyclo*hexene (4·3 g.), dichloro*cyclo*hexane (8·4 g.), and trichloro*cyclo*hexane (4·2 g.). Fractions (xii) and (xiii) comprised the chloro*cyclo*hexene but were not entirely free from dichloro-derivatives [Found for (xii): C, 61·1; H, 7·75; Cl, 31·1; reactive Cl, 23·1; *I.V.*, 205. Calc. for a mixture of 95·5% C_6H_9Cl and 4·5% $C_6H_{10}Cl_2$: C, 61·1; H, 7·7; Cl 31·2%; *I.V.*, 208. Found for (xiii): C, 60·4; H, 7·7; Cl, 31·6; reactive Cl, 23·5; *I.V.*, 204. Calc. for a mixture of 91·8% C_6H_9Cl and 8·2% $C_6H_{10}Cl_2$: C, 60·65; H, 7·7; Cl, 31·75%; *I.V.* 200].

1-Chloro*cyclo*hexene was prepared by the action of phosphorus pentachloride on *cyclo*hexanol-free *cyclo*hexanone (Skita and Ritter, *Ber.*, 1911, **44**, 674) and was freed from unreacted *cyclo*hexanone by treatment with semicarbazide hydrochloride; the purified liquid had b. p. 35°/13 mm. (Found: C, 61·6; H, 7·8; Cl, 30·55; reactive Cl, < 1; *I.V.*, 125. Calc. for C_6H_9Cl: C, 61·8; H, 7·8; Cl, 30·4%; *I.V.*, 218).

Monochlorodihydromyrcene was prepared by the action of chlorine on a considerable excess of dihydromyrcene (cf. Part IV), but it was difficult to separate the chlorination product from the excess hydrocarbon. The following fractions were examined: (i) b. p. 33—38°/13 mm. (Found: Cl, 8·25; reactive Cl, 7·5; *I.V.*, 315. Calc. for mixture of 40% $C_{10}H_{17}Cl$ and 60% $C_{10}H_{18}$: Cl 8·25%; *I.V.*, 329); (ii) b. p. 38—43°/13 mm. (Found: Cl, 13·3; reactive Cl, 11·8; *I.V.*, 298. Calc. for mixture of 64·5% $C_{10}H_{17}Cl$ and 35·5% $C_{10}H_{18}$: Cl, 13·3%; *I.V.*, 320); (iii) b. p. 43—46°/13 mm. (Found: C, 70·6; H, 10·0; Cl, 19·25; reactive Cl, 18·6; *I.V.*, 278. Calc. for mixture of 93·5% $C_{10}H_{17}Cl$ and 6·5% $C_{10}H_{18}$: C, 70·7; H, 10·1; Cl, 19·3%; *I.V.*, 299).

Two monochlororubbers were prepared as described in Part IV [Found: (*a*), Cl, 35·95 (34·6% substituted); reactive Cl, 24·4%. (*b*), Cl, 17·75 (all substituted); reactive Cl, 15·5%; *I.V*, 224].

Halogenation with Phenyliododichloride.—To purified rubber hydrocarbon * (5 g.) dissolved in carbon tetrachloride (300 c.c.) was added phenyliododichloride (19·2 g., 0·95 mol. per C_5H_8 unit) and the suspension was heated to boiling with stirring; a brisk reaction set in and a colourless homogeneous solution resulted. A little hydrogen chloride (0·1 g., corresponding to $<$ 4% substitutive reaction) was evolved. The product, polyisoprene dichloride (see p. 120), isolated by precipitation with alcohol, was a white, fibrous mass (10 g.), readily soluble in most rubber solvents (Found: C, 45·4; H, 6·0; Cl, 48·1; *I.V.*, 16; intrinsic viscosity $[\eta]$ in benzene, 2·125, indicating probable *M*, 127,000. Calc. for 96% additive reaction of 0·95 mol. reagent: C, 44·65; H, 5·9; Cl, 49·45%; *I.V.*, 17). Additive reaction to the extent of 98% was observed when acetone-extracted crepe rubber was brought to reaction in a similar manner but with benzoyl peroxide (4% of weight of rubber) present; when, however, quinol was substituted for the peroxide only 86% of the reagent was utilised in 30 mins. at the b. p., and 27% of the reacted phenyliododichloride chlorinated the rubber substitutively.

Action of Chlorine on Polyisoprene Dichloride.—Chlorine (2·1 g.) was passed slowly in bright light through a carbon tetrachloride solution (300 c.c.) of the dichloride (4 g.). The halogen did not react very readily and only 0·7 g. was consumed; a little hydrogen chloride (0·3 g.) was formed. The product was a white, fibrous substance (Found: Cl, 53·05; *I.V.*, 0; $[\eta]$ in benzene, 1·58, indicating probable *M*, 94,000. Calc. for substitutive reaction of 0·6 g. and additive reaction of 0·1 g. chlorine: Cl, 53·0%).

Halogenations with Sulphuryl Chloride.

Method.—The reagent was diluted with an equal volume of carbon tetrachloride and run into the solution of the olefin in carbon tetrachloride at the b. p. of the latter, in the dark, and in an atmosphere of nitrogen. For the absorption system two wash-bottles containing water and a third containing aqueous sodium hydroxide (5%) were used; in the first two bottles the bulk of the sulphur dioxide and all of the hydrogen chloride formed were absorbed, and any sulphuryl chloride carried over with the gaseous reaction products was hydrolysed to hydrochloric and sulphuric acids. The third bottle trapped any sulphur dioxide swept out of the aqueous solution. The sulphur dioxide was determined iodometrically, the sulphuric acid gravimetrically, and the hydrochloric acid volumetrically (dichlorofluorescein indicator) after oxidation of sulphur dioxide with hydrogen peroxide. From the amount of hydrogen chloride formed was deducted a quantity equivalent to the sulphuric acid found to allow for sulphuryl chloride hydrolysed in accordance with the equation $SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$, and from the remaining hydrogen chloride was calculated the extent of substitutive chlorination in accordance with the equation $RH + SO_2Cl_2 = RCl + HCl + SO_2$.

Chlorination of cyclo*Hexene in Presence of Peroxide.*—In Kharasch and Brown's preparation (*loc. cit.*) of dichloro*cyclo*hexane, b. p. 66—68°/13 mm. (Found: C, 47·2; H, 6·7; Cl, 46·1; reactive Cl, 0·4. Calc. for $C_6H_{10}Cl_2$: C, 47·05; H, 6·6; Cl, 46·35%), the sulphur dioxide formed corresponded to utilisation of 90% of the reagent and the hydrogen chloride formed corresponded to $<$ 5% substitutive reaction.

Chlorination of cyclo*Hexene in Presence of Antioxidant.*—Sulphuryl chloride (22·5 g.), reacting with peroxide-free *cyclo*hexene (50 g.) in the presence of quinol (0·2 g.), yielded after removal of excess *cyclo*hexene a liquid product (22·5 g.) together with sulphur dioxide (8·3 g., 78% utilisation of reagent in substitutive and additive reactions) and hydrogen chloride (0·82 g.) corresponding to 14% substitutive reaction; 5·5% of the reagent was swept out of the reaction flask. Distillation of the liquid product gave the following fractions: (i) b. p. 55—65°/13 mm. (5·9 g.); (ii) b. p. 65—70°/13 mm. (9·2 g.); (iii) b. p. $<$ 74°/0·002 mm. (2·4 g.); (iv) b. p. 74°/0·002 mm. (3·6 g.); (v) residue (0·5 g.). Redistillation of fraction (i) gave sub-fractions (vi) b. p. 40—65°/13 mm. (3·4 g.), containing unsaturated material, and (vii) b. p. 65—68°/13 mm. (2·3 g.), saturated to iodine chloride. Fractions (ii) and (vii), total 11·7 g., were mainly dichloro*cyclo*hexane (Found: C, 47·95; H, 6·7; Cl, 45·2%). Redistillation of fractions (iii) and (iv) gave the *chloride* of 2-*chloro*cyclo*hexyl sulphite*, b. p. 74°/0·002 mm.; some sulphur dioxide was liberated before its analysis could be carried out [Found: C, 34·2; H, 4·75; Cl, 33·65; S, 13·6. $C_6H_{10}Cl_2(SO_2)_{0·9}$ requires C, 34·2; H, 4·8; Cl, 33·65; S, 13·7%]. An identical liquid resulted from the action of thionyl chloride on *cyclo*hexanol at 0° (cf. Stähler and Schirm, *loc. cit.*). The chloride reacted with water with evolution of heat, liberating 1 mol. of hydrogen chloride and less than 1 mol. of sulphur dioxide, so yielding a liquid product which gave on distillation mainly 2-chloro*cyclo*hexanol (Found: C, 53·3; H, 8·3; Cl, 26·4; OH, 12·7. Calc. for $C_6H_{11}OCl$: C, 53·55; H, 8·25; Cl, 26·35; OH, 12·6%) and a non-volatile solid residue, believed to be *bis*-(2-*chloro*cyclo*hexyl) sulphite*, m. p. 92° from light petroleum (Found: C, 45·95; H, 6·5; Cl, 22·65; S, 10·2. $C_{12}H_{20}O_3Cl_2S$ requires C, 45·7; H, 6·4; Cl, 22·5; S, 10·15%).

Chlorination of cyclo*Hexene in Presence of Iodine.*—Sulphuryl chloride (16·7 g.), *cyclo*hexene (30 g.), and iodine (0·2 g.) required 1½ hours at 80° for completion of reaction and yielded a liquid product (15·5 g.) together with sulphur dioxide (6·4 g., 81% utilisation of reagent) and hydrogen chloride (1·28 g., 35% substitutive reaction of reagent utilised). The liquid gave the following fractions: (i) b. p. 30—60°/13 mm. (3·6 g.), (ii) b. p. 60—68°/13 mm. (10·2 g.): the latter fraction was mainly dichloro*cyclo*hexane. Fraction (i) was united with fraction (vi) of the preceding experiment; redistillation gave a main fraction, b. p. 52—55°/13 mm. (5·0 g.), which was principally 3-chloro*cyclo*hexene (Found: C, 59·2; H, 7·6; Cl, 32·9; reactive Cl, 25·7; *I.V.*, 182. Calc. for a mixture of 82·6% C_6H_9Cl and 17·4% $C_6H_{10}Cl_2$: C, 59·2; H, 7·6; Cl, 33·2%; *I.V.*, 180).

Peroxide-catalysed Chlorination of a Chloro-substituted Rubber $(C_5H_7Cl)_n$.—A solution in carbon tetrachloride of a chlororubber [(*a*), see above (Cl, 35·95%)], obtained by the action of chlorine on rubber (4·0 g.), was treated with sulphuryl chloride (9·0 g., 1·25 mols. per C_5H_8 unit) and benzoyl peroxide (0·2 g.) at 80° in a nitrogen atmosphere in the dark. Reaction was incomplete in 2 hours and there were formed in this time sulphur dioxide (3·75 g.), corresponding to 7·7 g. of reacted sulphuryl chloride (*i.e.*, 1·02 mols. per C_5H_8 unit), and hydrogen chloride (1·11 g.), corresponding to additive reaction of 3·75 g. of reagent (0·49 mol. per C_5H_8 unit) and substitutive reaction of 4·15 g. of reagent.

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* This was an oxygen-free hydrocarbon obtained by light-petroleum extraction of acetone-extracted crepe rubber from which the oxygenated fraction had been removed (Bloomfield and Farmer, *Trans. Inst. Rubber Ind.*, 1940, **16**, 69).

Peroxide-catalysed Chlorination of Dihydromyrcene.—Sulphuryl chloride (16·7 g.) and dihydromyrcene (44 c.c., 1 mol. reagent per $|\underset{4}{=}$) reacting in the presence of benzoyl peroxide (0·2 g.) yielded a liquid product (38 g.) together with sulphur dioxide (7·25 g.) and hydrogen chloride (0·2 g.). The liquid gave the following fractions on distillation : (i) dihydromyrcene, b. p. 55—58°/13 mm. (14·9 g.) ; (ii) b. p. $<$ 55°/0·2 mm., mainly dihydromyrcene (2·5 g.) ; (iii) b. p. 55—56°/0·2 mm. (14·5 g.) ; (iv) b. p. 56—60°/0·2 mm. (1·7 g.) ; (v) b. p. $<$ 74°/0·002 mm. (1·9 g.) ; (vi) 74—78°/0·002 mm. (2·5 g.) ; residue (1·2 g.). Fraction (iii) was *dihydromyrcene dichloride* (Found : C, 57·65 ; H, 8·6 ; Cl, 33·45 ; reactive Cl, 5 ; *I.V.*, 128. $C_{10}H_{18}Cl_2$ requires C, 57·4 ; H, 8·7 ; Cl, 33·9% ; *I.V.*, 122). Fraction (vi) had *I.V.* 74 and was probably mainly dihydromyrcene tetrachloride (see below).

Sulphuryl chloride (26·2 g. ; 2 mols.) reacted with dihydromyrcene (13·4 g. ; 1 mol.) in the presence of benzoyl peroxide (0·2 g.) to give a liquid product (27 g.) together with sulphur dioxide (11·35 g.) and hydrogen chloride (0·34 g.). Distillation of the liquid yielded *dihydromyrcene tetrachloride* (18·6 g.), b. p. 82—90°/0·002 mm. (Found : C, 43·35 ; H, 6·5 ; Cl, 50·0 ; *I.V.*, $<$ 2. $C_{10}H_{18}Cl_4$ requires C, 42·9 ; H, 6·5 ; Cl, 50·6%), together with a little liquid (0·8 g.) of lower b. p. and some residue (3·8 g.). Part of the dihydromyrcene tetrachloride crystallised on standing ; the crystals (from methanol) had m. p. 50° (Found : C, 42·9 ; H, 6·55 ; Cl, 50·7%).

Peroxide-catalysed Chlorination of Rubber.—The rubber (4 g.) (see footnote, p. 119) was dissolved in carbon tetrachloride (250 c.c.) under conditions precluding access of air, and allowed to react at 80° with sulphuryl chloride (7·8 g.) in the presence of benzoyl peroxide (0·1 g.) ; there were formed sulphur dioxide (3·5 g.) and hydrogen chloride (0·1 g.). The reaction product (8·0 g.), isolated by precipitation with alcohol, was indistinguishable from the *polyisoprene dichloride* described above (Found : C, 43·1 ; H, 5·7 ; Cl, 51·25 ; reactive Cl, 3 ; *I.V.*, 14 ; $[\eta]$ in benzene, 2·015, indicating probable *M*, 120,000. $C_5H_8Cl_2$ requires C, 43·1 ; H, 5·75 ; Cl, 51·15% ; *I.V.*, 0). This product was stable in air and at 80°.

From crepe rubber (10 g.) and sulphuryl chloride (10 g.) there were formed sulphur dioxide (4·4 g.), hydrogen chloride (2·2 g.), and a rubber-like product (12 g.), which was unstable on exposure to air or on heating (Found : Cl, 23·0 ; reactive Cl, 16·5. Calc. for 90% substitutive and 10% additive reaction : substituted Cl, 18·5 ; total Cl, 23·5%). From acetone-extracted crepe rubber (5 g.) and sulphuryl chloride (5 g.) there was similarly obtained 0·6 g. of hydrogen chloride, corresponding to 45% substitutive reaction.

Halogenation with N-*Bromosuccinimide.*

Bromination of Dihydromyrcene.—*N*-Bromosuccinimide (18 g., 1 atom Br per $C_{10}H_{18}$) and dihydromyrcene (17·7 c.c.) in carbon tetrachloride (100 c.c.) were kept at 77° in an atmosphere of nitrogen ; no hydrogen bromide was liberated. Distillation of the product, after separation of succinimide (9·9 g.), yielded a liquid fraction, b. p. 54°/0·1 mm., together with some unreacted dihydromyrcene and considerable residue. The liquid was *monobromodihydromyrcene* (Found : C, 55·2 ; H, 7·9 ; Br, 36·5 ; reactive Br, 36·2 ; *I.V.*, 226. $C_{10}H_{17}Br$ requires C, 55·3 ; H, 7·9 ; Br, 36·8% ; *I.V.*, 234).

Bromination of Rubber.—Reaction between *N*-bromosuccinimide (6·6 g., 1 atom Br per two C_5H_8 units) and acetone-extracted crepe rubber (5 g.) in carbon tetrachloride (300 c.c.) was complete in 30 mins., giving a reddish-brown solution ; no hydrogen bromide was liberated. As soon as the reddish-brown, rubber-like product (7·8 g.) was freed from solvent it could not be redissolved ; consequently the reactive bromine and the iodine value could not be directly determined. The preparation was therefore repeated in benzene solution and 10 c.c. portions of the solution were taken for these determinations. The bromo-rubber content of the solution was also determined by evaporation in a vacuum of a 10 c.c. portion, the residue being subsequently thoroughly extracted with methanol (Found : C, 55·5 ; H, 7·1 ; Br, 37·4 ; reactive Br, 35 ; *I.V.*, 155. $C_{10}H_{15}Br$ requires C, 55·8 ; H, 7·0 ; Br, 37·2% ; *I.V.*, 236).

The Action of Bromine on Rubber.—A solution of sol rubber (5·0 g.) in chloroform (350 c.c.) was cooled to between $-$ 30° and $-$ 40°, and a solution of bromine (11·8 g., 1·0 mol. per C_5H_8 unit) and iodine (0·1 g.) in carbon tetrachloride (100 c.c.) was added in the dark, with shaking, in an atmosphere of nitrogen. No hydrogen bromide was evolved during the addition or on bringing the gelled solution to room temperature. The insoluble, pale brown, resinous product (16·5 g. Found : Br, 69·0. Calc. for $C_5H_8Br_2$: Br, 70·1%) did not evolve hydrogen bromide at temperatues up to 80° although it darkened considerably.

Hydrogen bromide was formed in considerable quantity (0·6—0·8 g.) when rubber (5 g.) in carbon tetrachloride or carbon disulphide was treated at 0° with bromine (5·9 g., 0·5 mol. per C_5H_8 unit) in the same solvent, under various conditions permitting access or exclusion of light, moisture, and oxygen. When either chloroform or carbon tetrachloride containing alcohol (1%) was used as solvent no hydrogen bromide was liberated. The most rapid bromination took place in chloroform ; moreover, there was no separation of the brominated product even when a full molecular proportion of bromine per C_5H_8 unit was added. No change in *I.V.* and no liberation of hydrogen bromide were observed on heating solutions of partly brominated rubbers (0·5—0·8 mol. of bromine per C_5H_8 unit) at 80° for an hour.

For a rapid estimation of rubber hydrocarbon, the sample (acetone-extracted crepe rubber, 0·1 g.) was dissolved in chloroform (50 c.c.) and cooled to 0°. Approximately twice the theoretical quantity of bromine was added in chloroform solution of known concentration, and the excess was estimated by treatment with potassium iodide solution followed by volumetric estimation of the liberated iodine (Found : *I.V.*, by bromine addition, 357 ; *I.V.*, by Kemp's modification of the Wijs procedure, 360).

Corrigendum.—The fraction, b. p. 56—60°/0·01 mm., obtained by the chlorination of 1-methyl*cyclo*hexene (Part IV) was mainly trichloromethyl*cyclo*hexane (Found : Cl, 49·9. Calc for $C_7H_{11}Cl_3$: Cl, 50·2%) and not methyl*cyclo*hexene dichloride as formerly assumed.

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