178. *The Action of Chlorine on Isoprene.*

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WHILST much attention has been paid to the addition of halogens to conjugated systems, the action of chlorine on isoprene has not hitherto been investigated. The chlorination of butadiene in non-polar solvents, however, has been investigated by Muskat and Northrup (*J. Amer. Chem. Soc.*, 1930, **52**, 4043), who showed by ozonisation that in all cases the product was a mixture of the 1 : 2- and the 1 : 4-dichloride, b. p.'s 115° and 145°, respectively, together with the two stereoisomeric 1 : 2 : 3 : 4-tetrachlorobutanes; a similar result was obtained at — 75° in the absence of any solvent. Muskat and Huggins (*ibid.*, 1929, **51**, 2496) found that the only dichloride produced by the chlorination of 1-phenylbutadiene was the 3 : 4-compound, b. p. 125°/3 mm., as was demonstrated by ozonisation, the yield of dichloride depending both on the temperature, which was varied from — 80° to 150°, hydrogen chloride being lost at the higher temperatures, and on the extent of dilution, which decreased the amount of tetrachloride.

The action of bromine on 2-methylbutadiene has been investigated by Tilden (J., 1884, **45**, 410), Mokiewsky (*J. Russ. Phys. Chem. Soc.*, 1898, **30**, 1885), Ipatiew (*ibid.*, 1901, **33**, 540), Blaise and Courtot (*Bull. Soc. chim.*, 1906, **35**, 989), Bergmann (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 24), Staudinger, Muntwyler, and Kupfer (*Helv. Chim. Acta*, 1922, **5**, 756), and by Shephard and Johnson (*J. Amer. Chem. Soc.*, 1932, **54**, 4385). The first to assign the correct formula to isoprene dibromide was Bergmann, who proved that it had the

1 : 4-structure by ozonolysis, which Staudinger and his co-workers confirmed by its oxidation with permanganate first to the glycol, m. p. 127°, and then to bromoacetic acid.

The necessity of employing pure conjugated compounds in work on addition was first emphasised by Prévost (*Ann. Chim.*, 1928, **10**, 407). Accordingly, particular attention was paid to the purity of the hydrocarbon used in the present work.

Waterman and van Westen (*Rec. trav. chim.*, 1929, **48**, 1084) have given a summary of the methods of purifying isoprene adopted by previous workers. Commencing with crude 2-methyl-Δ^2-butene, they themselves synthesised an isoprene with a theoretical hydrogenation value. Farmer and Warren (J., 1931, 3221), using the Diels–Alder method as a test of chemical homogeneity, found that the purest isoprene was obtained by the catalytic dehydration with aniline hydrobromide of isoprene alcohol, derived from limonene. They found it necessary to wash the product at least twenty times with water, to remove traces of the alcohol, before constant physical values could be obtained, and they admitted that the method was long and laborious. A purified isoprene has been prepared by Whitby and Crozier (*Canadian J. Res.*, 1932, **6**, 212) by treatment of fractionated isoprene tetrabromide with zinc dust in alcohol, but only the b. p. has been given and no other test of purity made.

The method of preparation of pure isoprene from its sulphone, mentioned by Bassett and Williams (J., 1932, 2324), has been further elaborated, and is here described in detail. The method is simpler than that of Farmer and Warren, although still laborious, and gives a product of high purity.

The combination of isoprene with gaseous sulphur dioxide was first mentioned by the Badische Anilin- und Soda-Fabrik A.-G. (*German Pat.*, 236,386, 1910), the product being described as partially soluble in water, but the bulk as amorphous. The product was found to be decomposed by heat into sulphur dioxide and the original hydrocarbon. Bruin (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 585), Ostromisslenski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1983), Matthews and Strange (*British Pats.*, 6897, 18.3.14; 5073—4, 1.4.15), and Eigenberger (*J. pr. Chem.*, 1930, **127**, 307) have further investigated the product. The last-named author obtained a 60% yield by treating isoprene for five hours with ether saturated with sulphur dioxide, the optimum temperature, 100°, being reached as rapidly as possible to avoid the setting-in of a colloidal separation. He found that the product, m. p. 63—63·5°, was best recrystallised from hot water; it decomposed at 120° to give isoprene and sulphur dioxide, the reaction being almost complete at 135°, and he proved it to be 2-methyl-Δ^2-butene-1 : 4-sulphone.

It was found by Bassett and Williams, though not published, that, when about 2 g. of crude isoprene were mixed with four times its weight of liquid sulphur dioxide in a well-stoppered vessel, a 75% yield of the sulphone was obtained after 1 day in ice and 5—6 days at the ordinary temperature. This method has now been carried out on a considerably larger scale, and it has the advantage over previous methods in that the yield is increased, while no amorphous compound and very little tar is obtained, even if crude isoprene, from rubber, of only 60—70% purity is used. The presence of increasing amounts of water or alcohol is found to give increasing yields of amorphous compound. Excepting that of Eigenberger, the other methods of preparing the sulphone gave considerable amounts of this contaminating product, while his suffers from the disadvantage of requiring either a sealed tube or an autoclave. In the present method the isoprene was regenerated by heating the recrystallised sulphone to 120—135°. Its homogeneity was confirmed by the maleic anhydride method of Farmer and Warren (*loc. cit.*).

It was found that, when chlorine gas was passed into a solution of isoprene in carbon tetrachloride, a considerable amount of hydrogen chloride was evolved, and for that reason, in the present work, the pure isoprene (one mol.) was dissolved in carbon tetrachloride, and chlorine (one mol.) in the form of a solution in the same solvent was slowly added, the mixture being continuously stirred and well cooled. This appears to be the mildest possible means of adding chlorine at the temperature employed, because its concentration is maintained so very low. On fractionation of the residue left after removal of the solvent, two main products were obtained, which have been shown to be 1-*chloro*-2-*methylbutadiene*, $CHCl{:}CMe{\cdot}CH{:}CH_2$, b. p. 50·4°/100 mm., and 1 : 4-*dichloro*-2-*methyl*-Δ^2-*butene*,

$CH_2Cl·CMe⁚CH·CH_2Cl$, b. p. 93°/50 mm. Indications of the presence of a lower-boiling dichloride, b. p. about 60°/50 mm., in small amount were also obtained. The structure of this compound has not yet been determined, but it appears to become purified on standing with free access of air, owing to removal of the monochloride by polymerisation and oxidation. Besides these substances, an undistillable residue was obtained. This seemed to consist of products of the polymerisation and decomposition of the monochloride, mixed with the dichloride, for the proportion of the undistillable residue increased when the products of chlorination were kept for any appreciable time before fractionation. In no case did the chlorine content of the liquid boiling higher than the dichloride exceed that of the dichloride, but decreased with increase in b. p. This fact further showed the absence of any higher chlorinated derivative in any appreciable quantity, when isoprene was chlorinated by the method described.

The structure of the dichloride was determined by ozonolysis, both in chloroform and without solvent. No formaldehyde could be detected on decomposition of the ozonide with water, and on extraction with ether the only product which could be identified was monochloroacetone, thus proving that the dichloride was the 1 : 4. The absence of any appreciable amount of chloroacetaldehyde in the ethereal extract was found to be due to the formation of a water-soluble hydrate, $2CH_2Cl·CHO,H_2O$ (Natterer, *Monatsh.*, 1882, **3**, 459), although sufficient was obtained to give a fuchsin test. Titration of the decomposed ozonide in aqueous solution with potassium hydrogen sulphite solution disclosed the presence of the carbonyl group in almost quantitative yield corresponding to the formation of monochloroacetone and chloroacetaldehyde in equivalent proportion. The chloroacetaldehyde was identified as chloroacetic acid by oxidation with neutral permanganate solution, and it was established by a control experiment that chloroacetone on oxidation under these conditions gave acetic acid, and no appreciable amount of chloroacetic acid. Acetic and chloroacetic acids were finally separately identified in a proportion showing that equivalent amounts had been formed, thus confirming the 1 : 4-structure of the dichloride.

A dichlorohydrin, corresponding to the dibromohydrin obtained by Bergmann (*loc. cit.*) and by Staudinger, Muntwyler, and Kupfer (*loc. cit.*), *viz.*, 1 : 4-*dichloro*-2 : 3-*dihydroxy*-2-*methylbutane*, was prepared by the method of the latter workers, and had m. p. 106·5° (corr.).

That the dichloride was a true addition product was shown by the fact that, on reduction with powdered zinc in alcohol (Thiele, *Annalen*, 1899, **308**, 333), it gave isoprene in good yield, but in absence of diluent, a violent reaction occurred on warming the dichloride with zinc dust (compare Muskat and Huggins, *loc. cit.*) and then no isoprene could be detected. This is another possible method of preparing pure isoprene, since the sulphone obtained from the product was found to give the correct m. p. without recrystallisation, although contaminated with amorphous compound, for the alcohol which caused the formation of this compound could have been previously removed by washing with water. The stability of the dichloride was shown by the fact that the refractive index remained unaltered after this substance had been kept for two months in a loosely stoppered bottle.

In the bromination of isoprene, Staudinger, Muntwyler, and Kupfer (*loc. cit.*) obtained no monobromide, although Bergmann (*loc. cit.*) had previously found one, which he considered to be an allene derivative. The monochloride obtained in the present work, however, was found to be a conjugated compound, its structure being established by its combination with α-naphthaquinone and oxidation of the product with air in alkaline solution to the known 1-chloro-2-methylanthraquinone, m. p. 171° (Keimatsu and Hirano, *J. Pharm. Soc. Japan*, 1929, **49**, 140) by the method of Carothers and Coffman (*J. Amer. Chem. Soc.*, 1932, **54**, 4071).

Since the isoprene here used had been purified by means of its sulphone, it was thought that the monochloride might possibly be capable of being similarly purified, and, accordingly, it was treated with liquid sulphur dioxide in excess under the same conditions. A white crystalline compound was obtained, m. p. 73° (corr.), which, when finely divided, provoked intense sneezing, and in solution caused irritation of the skin. This compound, on being heated, gave sulphur dioxide and the original monochloride, being so proved to be

1-*chloro-2-methyl-Δ^2-butene-*1 : 4-*sulphone,* and its formation confirms the conjugated structure of the monochloride.

Since it is well known that, at low temperatures, chlorine adds on to unsaturated aliphatic compounds, and does not substitute, the monochloride most probably arises by loss of hydrogen chloride from an unstable, more highly chlorinated derivative. This might be the 1 : 2-addition product, an unsaturated tertiary chloride, a series which is known to have a tendency to isomerise or decompose.

EXPERIMENTAL.

The Preparation and Purification of Isoprene.—The crude isoprene was prepared by the rapid distillation of rubber in 500 g. lots, as described by Bassett and Williams (*loc. cit.*). The fraction, b. p. 30—45°, was poured into a bottle with a well-fitting vaselined stopper, immersed in ice-salt, and 3—4 times its weight of liquid sulphur dioxide was added. The whole was left in ice for 24 hours and then at room temperature for 5 days. No separation of crystals occurred, but, when only a slight excess of sulphur dioxide was used, the sulphone crystallised from the sulphur dioxide as very large rhombic plates. The sulphur dioxide was then allowed to evaporate and was finally completely removed at 50° under reduced pressure, together with the impurities and unchanged isoprene. The crude sulphone remaining was twice recrystallised from hot water (the solubility being about 50 g./100 c.c.), filtered off, and washed with cold water. The washings were added to the mother-liquor, which was concentrated to give further crops of crystals, the final crops being again recrystallised. It was found advantageous to allow part of the sulphone to separate below the hot aqueous solution as an oil, since this absorbed, and so removed, the tar. On cooling, crystals formed in the aqueous layer, and these were separated for recrystallisation. They formed colourless and needle-shaped rhombic plates, m. p. 63·5° (corr.), and were first dried in the air and then in a vacuum over calcium chloride. By this means four distillations of rubber (2000 g.) gave about 220 g. of the pure sulphone. This was decomposed by heating to 120—135°, the isoprene and sulphur dioxide being immediately bubbled through almost saturated aqueous sodium hydroxide kept at about 70°, and the isoprene collected in a flask cooled in ice-salt. The product, which smelt slightly of sulphur dioxide, was washed four times with almost saturated sodium hydroxide solution and finally with water till neutral to phenolphthalein. It was dried over calcium chloride and twice distilled from sodium wire. Only a trace of residue was left after distillation, the b. p. range never exceeding 1°. The yield of pure isoprene after this treatment was 80—90%, calculated on the sulphone. The liquid had a pleasant ethereal odour, different from the rather fish-like smell of isoprene that has been merely fractionated. The isoprene used in the determinations of the physical properties had several additional washings with water and one more distillation, the first and the last portion being rejected. It was found to be chemically homogeneous by the method of combination with pure maleic anhydride in pure, dry, sulphur-free benzene, the procedure followed being exactly as described by Farmer and Warren (*loc. cit.*), the product having an unchanged m. p. of 63·5—64° (corr.).

A sample of isoprene thus purified (120 g.) boiled completely between 33·9° and 34·3° on being heated cautiously with a micro-burner. The refractive index was determined by means of a water-jacketed standardised Pulfrich refractometer, and the density was determined in a 10 c.c. Hartley pyknometer and corrected for buoyancy, the measurements being carried out on the freshly distilled liquid. The results obtained and those of previous workers are summarised in the following table :

	B. p.	$d_{4^\circ}^{20^\circ}$.	$n_C^{20^\circ}$.	$n_D^{20^\circ}$.	$n_F^{20^\circ}$.	$[R_L]_D$.	Exaltation.
Waterman and van Westen	34·5—35·0°/762 mm.	0·6806	1·4154	1·4194	1·4301	25·29	0·93
Farmer and Warren ...	33·9—35·3°/750 mm.	0·6806	1·4165	1·4207	1·4315	25·34	0·98
Whitby and Crozier	33·4—33·9°/744 mm.	—	—	—	—	—	—
Present work	33·9—34·3°/760 mm.	0·6806	1·4176	1·4214	1·4328	25·38	1·02

When allowance is made for the difference in pressure, the b. p. of the present product is slightly lower than those recorded by the previous workers.

Chlorination of the Isoprene.—Carbon tetrachloride was shaken with almost saturated sodium hydroxide solution, washed with water, dried over calcium chloride and then over phosphoric oxide, and distilled, the middle fraction only being retained. Chlorine, prepared by the action of concentrated hydrochloric acid on permanganate, was passed through water, through concentrated sulphuric acid, and finally into 1001 g. of the carbon tetrachloride cooled in ice (1 g. of the solvent was lost during the solution of the gas under the conditions obtaining); 130 g. of chlorine could thus be dissolved in 1000 g. of carbon tetrachloride. To a weighed amount of isoprene (about 100 g.), purified as described above, together with some carbon tetrachloride, mechanically stirred and cooled in ice–salt, the calculated amount of chlorine solution was added during about 4 hours, hydrogen chloride being evolved. The bulk of the carbon tetrachloride was then removed at 48°/300 mm., and the product repeatedly fractionated under reduced pressure in an all-glass Pyrex flask and column, the latter being filled with rings and fitted with a small dropping-funnel whereby successive fractions could be added without affecting the pressure. Considerable loss of material, especially of the monochloride, was sustained during the fractionation, which was inevitably long and laborious. For general purposes, the mono- and dichlorides were finally collected over a 1° range.

Analysis of the crude product by the method of Young and Fortey (J., 1902, **81**, 752), allowance being made for losses, and on the assumption that the monochloride had been formed by the decomposition of a dichloride, showed that the yield of monochloride was 38%, that of the lower-boiling dichloride 6%, and that of the higher-boiling dichloride 45%, the remaining 11% being undistillable residue.

The Structure of the Monochloride.—From 100 g. of isoprene, about 8 g. of monochloride distilling over a 1° range were obtained. This monochloride (6 g.) was heated with 3·5 g. of α-naphthaquinone at about 80° for 4 hours in nitrogen. The bluish product obtained on cooling was washed with absolute methyl alcohol several times and crystallised from aqueous acetone, giving yellow needles, m. p. 141—143°. Recrystallised several times from aqueous acetone and finally from pure acetone, these became very pale yellow and had m. p. 146° (corr.), mixed m. p. with α-naphthaquinone 91—97°. The m. p. was unaltered by further recrystallisation from alcohol (charcoal), but the 1-*chloro*-2-*methyl*-1 : 4 : 4*a* : 9*a*-*tetrahydroanthraquinone* then formed white needles (Found: C, 69·2; H, 4·9; Cl, 13·6. $C_{15}H_{13}O_2Cl$ requires C, 69·1; H, 5·0; Cl, 13·6%). It was oxidised by air in alcoholic sodium hydroxide (Carothers and Coffman, *loc. cit.*); the product on recrystallisation, first from glacial acetic acid and then from alcohol, had m. p. 171—172° (corr.), identical with that of the preparation of Keimatsu and Hirano (*loc. cit.*).

Isoprene Monochloride Sulphone.—When the monochloride was treated with excess of liquid sulphur dioxide under the same conditions as described in the case of isoprene, there resulted a dark tarry solid. This, fractionally crystallised from ether, gave fine white crystals, m. p. 73° (corr.). It is, however, best crystallised from water, which effectively separates the tar, and it forms rhombic plates; the sulphone decomposes in boiling aqueous solution, giving a tar, as the corresponding isoprene derivative does (Eigenberger, *loc. cit.*), and therefore the solution was concentrated by evaporation under reduced pressure. When an ethereal solution was treated with alcohol, a colloidal solution resulted which remained uncoagulated when boiled. The 1-*chloro*-2-*methyl*-Δ^2-*butene*-1 : 4-*sulphone* (Found: C, 35·8; H, 4·2; Cl, 21·4; S, 19·2. $C_5H_7O_2ClS$ requires C, 36·0; H, 4·2; Cl, 21·3; S, 19·2%) was easily soluble in the common organic solvents, but only slightly in the paraffins. The solubility was about 7·2 g. per 100 c.c. of water at 75° and 2·4 g. at 15°. The pure sulphone gave a colourless solution in cold concentrated sulphuric acid. It decomposed at 125°, evolving sulphur dioxide.

Purification of the Monochloride.—The sulphone (17·8 g.) was heated under a pressure of 100 mm., since, in this case, the decomposition products could not be scrubbed with sodium hydroxide solution. The temperature rose to 140° and 8·4 g. (77% yield) of distillate were collected. This was washed with sodium hydroxide solution and with water, dried over calcium chloride, and distilled; the resulting colourless 1-*chloro*-2-*methylbutadiene* (Found: C, 58·4; H, 7·0; Cl, 34·6. C_5H_7Cl requires C, 58·5; H, 6·9; Cl, 34·6%) had a pleasant smell like that of isoprene, and a constant b. p. of 50·4°/100 mm. The middle fraction was used for the determination of its physical constants, $d_{4°}^{20°}$ 0·9710, $n_D^{20°}$ 1·4792, $[R_L]_D$ 29·95 (calc., 29·22), b. p. 107°/760 mm. (with slight polymerisation). The monochloride dissolved to a dark brown solution in cold concentrated sulphuric acid. When 4·1 g. of this monochloride were treated with liquid sulphur dioxide as before, there resulted 6·25 g. (94% yield) of white solid, m. p. 71° (corr.), containing no tar, which must therefore have previously been caused by the impurities in the crude monochloride. On recrystallisation of the solid from hot water, there was left a small amount of insoluble amorphous substance. The identity of the regenerated liquid with the original monochloride was then confirmed by a mixed m. p. of its recrystallised sulphone with the original sulphone, *i.e.*, 73° (corr.). Thus, isoprene and its monochloride can be preserved in a form from which they can easily be regenerated, a convenience not afforded by the other methods of purification.

Polymerisation of the Monochloride.—A sample (0·2 g.) of the monochloride, purified by fractionation only, after being kept in a sealed tube with merely a trace of air for 70 days, had not acquired colour but had suffered increase in viscosity, and in refractive index from $n_D^{20^\circ}$ 1·4742 to 1·4810, so indicating that polymerisation had occurred. Another sample of the same liquid kept in a loosely stoppered bottle, however, gave a considerably more rapid rise in refractive index, $n_D^{20^\circ}$ after 14 days 1·4820 and after 70 days 1·5063, thus showing that oxygen was accelerating the polymerisation and forming oxidation products. It had also increased considerably in viscosity, and become yellowish-brown. Analysis showed the presence of oxygen [Found : C, 55·8; H, 6·6; Cl, 33·1; O (by diff.), 4·5%]. After 6 months it gave a black sticky solid of almost the same composition, showing that little, if any, more oxygen had been absorbed {Found : C, 56·2; H, 6·6; Cl, 32·1; O (by diff.), 5·1. This is approximately of the composition $[(C_5H_7Cl)_3O]_x$, which requires C, 55·6; H, 6·5; Cl, 32·9; O, 5·0%}. It has been shown by Whitby and Gallay (*Canadian J. Res.*, 1932, **6**, 280) that the ability of a conjugated diene to form a synthetic rubber depends on the presence of at least three terminal hydrogen atoms, a condition which is fulfilled by this new monochloride, whose rate of polymerisation is comparable with that of isoprene.

The Structure of the Higher-boiling Dichloride.—About 38 g. of this compound, boiling over a 1° range, were obtained from 100 g. of isoprene.

Chloroform was shaken several times with water, allowed to stand with concentrated sulphuric acid, separated, kept over ignited sodium carbonate, and finally distilled from phosphoric oxide, the middle fraction only being collected for use. The dichloride (23·5 g.) was dissolved in 50 g. of this chloroform and subjected to the action of 0·33% (by vol.) ozonised oxygen for 18 hours at 0°. The chloroform was then removed under reduced pressure, and the viscous oily ozonide treated with water and warmed to 75—80°. No formaldehyde could be detected and no volatile products were evolved, thus indicating that the dichloride was probably the 1 : 4. When an aliquot part of a sufficiently dilute solution of the product of the hydrolysis of the ozonide was treated with excess of standard potassium hydrogen sulphite solution and back-titrated with standard iodine, the presence of the carbonyl group in 99% yield was ascertained. The presence of the $CH_3\cdot CO\cdot C\vdots$ group in solution was shown by testing with iodine and dilute alkali, iodoform being formed and identified by the addition of pyridine, when a red colour developed in the pyridine layer above the alkaline iodoform. Repeated extraction of the original aqueous solution from the ozonide with ether and distillation of the dried ethereal layer gave a trace of liquid boiling at 85—86° (b. p. of chloroacetaldehyde), which responded to the fuchsin test for aldehydes, and an irritating liquid, b. p. 116—121° (monochloroacetone, b. p. 118—119°). When the latter was treated with a dilute solution of benzenediazonium chloride and sodium acetate in excess at 0° for 24 hours, it gave a tarry solid, which, on being filtered off, washed with water, and repeatedly crystallised from alcohol, gave a solid, m. p. 135—136°, and the same mixed m. p. with a sample of the phenylhydrazone of pyruvyl chloride (Favrel, *Bull. Soc. chim.*, 1927, **41**, 1494) prepared in the same way from authentic monochloroacetone, thus showing that the dichloride was the 1 : 4-addition product.

This was confirmed by oxidation of the product of hydrolysis of the ozonide with permanganate. Since no record could be found in the literature of the action of permanganate on monochloroacetone, 100 g. of this ketone were dissolved in 100 c.c. of water and treated with 228 g. of potassium permanganate, added in small portions with shaking. The manganese oxides were filtered off, and the filtrate was decolorised with sulphur dioxide, and repeatedly extracted with ether. On distillation of the dried ethereal extract, the only product which could be identified was acetic acid, by its smell, b. p., and by the m. p. and mixed m. p. of its anilide, 114°. Again, when 12 g. (0·2 mole) of acetic acid and 18·9 g. (0·2 mole) of chloroacetic acid were dissolved in 50 c.c. of water and the solution was extracted once with an equal volume of ether, there were recovered from the dried extract 5·7 g. of acetic acid and 11·8 g. of chloroacetic acid. This gives the proportion in which the acids are extracted from a solution containing equivalents.

The dichloride (25 g.) was ozonised in absence of solvent, the ozonide decomposed with warm water, and an excess of solid potassium permanganate added in small amounts with agitation. The manganese oxides were filtered off, and the filtrate was extracted with ether. The product after removal of the ether weighed 13·8 g. On distillation, this gave 4·0 g. up to 152°, 7·8 g. from 152° to 190°, and 1·5 g. of an undistillable residue, the first two fractions being in the expected proportion. Redistillation of the lower gave acetic acid, identified as before; the higher on redistillation gave a distillate, b. p. 184—186°, which solidified on cooling, m. p. 57—60° and mixed m. p. 59—61° with pure chloroacetic acid (62°). This was confirmed by converting the acid by means of phosphoric oxide (Cech, *Ber.*, 1877, **10**, 1376) into its anilide, m. p. and mixed m. p. 134° after crystallisation from hot water and then from alcohol–ether.

1 : 4-*Dichloro-2-methyl-*Δ^2*-butene* (Found : C, 43·0; H, 5·8; Cl, 51·1. $C_5H_8Cl_2$ requires C, 43·2; H, 5·8; Cl, 51·0%), b. p. 93°/50 mm. and 56°/10 mm., $n_D^{20°}$ 1·4932, $d_{4°}^{20°}$ 1·1526 (both determined with a constant-boiling middle fraction), $[R_L]_D$ 35·05 (calc., 34·56), is a colourless sharp-smelling liquid, with lachrymatory properties; it gives a yellowish-brown solution in cold concentrated sulphuric acid.

The liquid, obtained in the chlorination of isoprene, boiling higher than 1 : 4-dichloro-2-methyl-Δ^2-butene gave the following results on analysis : b. p. 104°/50 mm., Cl, 49·8; b. p. 107°/50 mm. (last drops of distillate), Cl, 47·9; residue, Cl, 39·7, 40·0%.

Preparation of the Dichlorohydrin.—The 1 : 4-dichloride (19 g.) was oxidised with potassium permanganate (14 g.) and water (2·5 c.c.) in pure acetone at − 5° by Staudinger's method (*loc. cit.*). On removal of the acetone, after filtration of the manganese oxides, and distillation, 4·8 g. of unreacted dichloride were recovered ($n_D^{20°}$ 1·4920), leaving a residue (6·6 g.), which on recrystallisation from ether gave colourless needles, m. p. 106·5° (corr.), of 1 : 4-*dichloro-*2 : 3-*dihydroxy-2-methylbutane* (Found : C, 34·8; H, 5·8; Cl, 41·0. $C_5H_{10}O_2Cl_2$ requires C, 34·7; H, 5·8; Cl, 41·0%). Treatment of the manganese oxides with water and sulphur dioxide, and extraction with ether, as advised by Staudinger for the dibromohydrin, gave only a very small additional amount of the impure product. The pure crystals gave a colourless solution in concentrated sulphuric acid.

Treatment of the Dichloride with Zinc.—When 15 g. of the dichloride and 30 g. of zinc dust were gently warmed, a violent reaction ensued, the dichloride decomposed with blackening, and hydrogen chloride was copiously evolved. No isoprene could be detected in the product.

A solution of the dichloride (22 g.) in alcohol (50 c.c.) was run dropwise on to 45 g. of zinc dust in 100 c.c. of nearly boiling alcohol. The product was distilled, the distillate being collected up to 78° and condensed in ice–salt. On fractionation, the initial b. p. was 33·9°/760 mm., that of pure isoprene. The distillate so collected up to 40° weighed 8·3 g., a yield of 77%. On treatment of 7·5 g. of this with liquid sulphur dioxide, there resulted 11·8 g. of white sulphone, which, owing to the alcohol, contained some insoluble amorphous product. The sulphone, m. p. 63·5°, remained unchanged on recrystallisation from water, and gave a mixed m. p. of 63·5° with authentic isoprene sulphone.

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