NOTE.

The Action of Hydrogen Chloride on Isoprene. By A. J. Ultée.

Jones and Chorley (*J.*, 1946, 832) stated that " addition of hydrogen chloride to isoprene occurs in the 1 : 4-position ", but it is now found that the addition occurs primarily in the 1 : 2-position, the product being isomerised by the action of the hydrogen chloride. There is no doubt that, under the conditions used by those investigators, 1-chloro-3-methylbut-2-ene is the chief product, but other investigators have obtained different results. By reaction at 0° between hydrogen chloride and isoprene—probably less than an equivalent quantity—Bouchardat (*Compt. rend.*, 1879, **89**, 1117) obtained, besides unchanged isoprene, a product, three-quarters of which boiled between 86° and 91°, with no appreciable higher-boiling fraction. Aschan (*Ber.*, 1918, **51**, 1303), on the other hand, obtained a product of b. p. 107—110° (slight decomp.) and suggested that Bouchardat's result was due to the presence of 2-methylbut-2-ene in his isoprene, from which, Aschan believed, 2-chloro-2-methylbutane, b. p. 86°, had been formed. The objection to this supposition, however, is, not only that Bouchardat had so large a yield, but the far more important fact that his product was unsaturated, and that it added on two atoms of bromine to afford $C_5H_9ClBr_2$.

Claisen, Kremers, Roth, and Tietze (*J. pr. Chem.*, 1922, **105**, 76) obtained a mixture of a large quantity of primary hydrochloride and a small amount of the lower-boiling, 2-chloro-2-methylbut-3-ene : this means that both 1 : 4- and 1 : 2-addition took place.

By using only $\frac{2}{3}$ instead of 1 equiv. of hydrogen chloride, the author obtained an appreciable amount of this low-boiling compound : on fractionation under ordinary pressure unchanged isoprene is first obtained, followed by a fraction of b. p. 79—83° (50—55% of the theoretical amount calculated on the hydrogen chloride used) ; further distillation in a vacuum then afforded a 20% yield of the compound reported by Jones and Chorley.

Similar results were obtained both with the crude isoprene produced by pyrolysis of rubber (isoprene content, by maleic anhydride test, about 87%) and with isoprene purified through the sulphone.

According to Markovnikov's rule, there are four possible mono-addition products, *viz.*, 1-chloro-3- and -2-methylbut-2-ene (I and II, respectively), 3-chloro-2-methylbut-1-ene (III), and 2-*chloro*-2-*methylbut*-3-*ene* (IV), all except the last being known. Jones and Chorley's compound is (I) ; Tischtschenko (*Chem. Zentr.*, 1937, I, 572) has proved the structure of (II), b. p. 110°/760 mm.; and according to Burgin, Engs, Croll, and Hearne (*Ind. Eng. Chem.*, 1939, **31**, 1413) (III) boils at 93·8°/760 mm. Hence only (IV) is left for the new compound, this being the only hydrochloride with a tertiary chlorine atom, which is compatible with the low b. p. Tischtschenko has commented on the easy transition from (III) to (II). In the same way, the new compound (IV) has a tendency to pass over into (I), for instance on boiling; at low temperatures hydrogen chloride strongly accelerates the conversion, which would explain why Jones and Chorley did not isolate the compound, though it was potentially in their reaction mixture. By working under similar conditions, *i.e.*, by using 1 equiv. of hydrogen chloride, at least 5% of the low-boiling product could be obtained in addition to their main product.

By addition of bromine to (I) and (IV), two different compounds were obtained. Further details will be given later respecting a number of halogen compounds derived from (I) and (IV), but it may be stated here that 3 : 4-dichloro-2-methyl-but-1-ene, b. p. 63·5—64·5°/50 mm., results from chlorination of Jones and Chorley's compound with sulphuryl chloride in the presence of quinol, the former compound having been produced by other means by Petrov (*Bull. Soc. chim.*, 1946, 4D). This compound is identical with the dichloride of low b. p. which Jones and Williams (*J.*, 1934, 832) obtained when chlorinating isoprene : they mention only b. p. 60°/50 mm.

Hence 1 : 2-addition may also take place on chlorination, be it only as a minor side reaction.

Experimental.—Preparation. Dry hydrogen chloride was bubbled through isoprene, to which ether had been added (6 g. to 50 g. of isoprene) to increase the solubility of the hydrogen chloride. The tared glass bottle containing the isoprene was cooled in acetone–carbon dioxide, care being taken not to let the temperature of the contents rise above − 15°. After $\frac{2}{3}$ equiv. of the gas had been absorbed, the reaction mixture was set aside at low temperature overnight. It was neutralized with anhydrous potassium carbonate, dried with calcium chloride, and distilled at ordinary pressure, a little calcined potassium carbonate being placed in the distilling flask. After the unchanged isoprene and the ether had passed over, the temperature rose rapidly ; the fraction of b. p. 79—83° was collected separately and redistilled in a vacuum.

Properties. If 2-*chloro*-2-*methylbut*-3-*ene* (Found : Cl, 33·9, 34·1. C_5H_9Cl requires Cl, 33·9%) is kept at its b. p., the temperature of the liquid rises gradually. Under reduced pressure the compound can be distilled unchanged ; b. p. 79·5—80°/760 mm., 32°/120 mm., $d_{2^\circ}^{20^\circ}$ 0·8855, $n_D^{20^\circ}$ 1·4190 ; $[R_L]_D$ 29·81 (Calc. : 29·69). In the presence of hydrogen chloride, conversion into Jones and Chorley's compound takes place at low temperature : dry hydrogen chloride (0·5 g.) was passed into 2-chloro-2-methylbut-3-ene (10 g.) cooled in ice–salt, and after standing overnight the mixture was neutralized, dried, and distilled ; the main fraction had b. p. 111—113·3°, $d_{20^\circ}^{20^\circ}$ 0·9300, $n_D^{20^\circ}$ 1·4480. Jones and Chorley give $d_{4^\circ}^{15^\circ}$ 0·9380, $n_D^{20^\circ}$ 1·4450.

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